



TITLE:

New Aspects of Reactions of Thiocarbonyl Compounds with Trialkyl Phosphites(Dissertation_全文)

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CITATION:

Kawase, Tokuzo. New Aspects of Reactions of Thiocarbonyl Compounds with Trialkyl Phosphites. 京都大学, 1978, 工学博士

ISSUE DATE:

1978-05-23

URL:

<https://doi.org/10.14989/doctor.k2065>

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NEW ASPECTS OF REACTIONS OF THIOCARBONYL COMPOUNDS WITH TRIALKYL PHOSPHITES

Tokuzō Kawase

1978

Department of Synthetic Chemistry
Kyoto University

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PREFACE

The present thesis is the collection of the studies carried out under the direction of Professor Zen-ichi Yoshida at the Department of Synthetic Chemistry of Kyoto University during 1973-1978. The thesis is concerned with the aspects of the reactions of thiocarbonyl compounds with phosphites.

The author wishes to express his grateful gratitude to Professor Zen-ichi Yoshida. His kind guidance, precious comments and criticisms during the course of this work are sincerely appreciated.

The author further wishes to express his deep thanks to Associate Professor Shigeo Yoneda for his enthusiastic interest, variable discussions and encouragement throughout this work.

The author's thanks are also due to Associate Professor Hisanobu Ogoshi and Dr. Yoshinao Tamaru for their helpful discussions and suggestions. The author is also indebted to Messrs. Hideki Murata, Mikio Inaba, Seiji Sugiyama and Yutaka Yasuda for their active collaborations. Valuable discussions with the author's colleagues are gratefully acknowledged.

Finally, the author thanks his parents for their affectionate encouragement throughout the work.

Tokuzō Kawase

March, 1978

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PUBLICATION LIST

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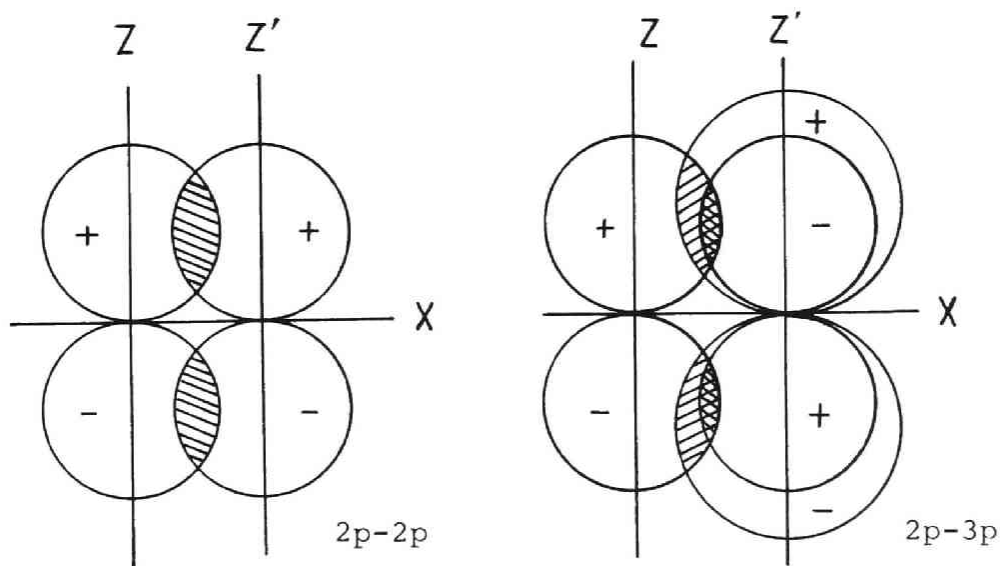
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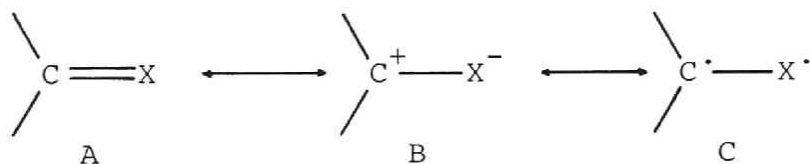
INTRODUCTION

During over the last one decade, especially the last half decade, remarkable developments of the chemistry¹ of thiocarbonyl compounds have brought exciting results about their reaction behaviors and the importance as the synthetic intermediates.

Bond energies of the carbon-oxygen double bond in carbon dioxide and the carbon-sulfur double bond in carbon disulfide are 192 and 123 Kcal/mole, respectively. Since bond energies of general carbon-oxygen and carbon-sulfur single bonds are 85.5 and 65 Kcal/mole, respectively, π -bond energy for carbon-sulfur bond is smaller than that for carbon-oxygen by about 50 Kcal/mole. The difference is undoubtedly due to the low efficiency of 2p-3p π -overlapping of carbon-sulfur bond in comparison with that of 2p-2p of carbon-oxygen bond. Because of the inherent antibonding interactions, as shown below, π -bonds from 2p and 3p orbitals are less favorable than two 2p orbitals.

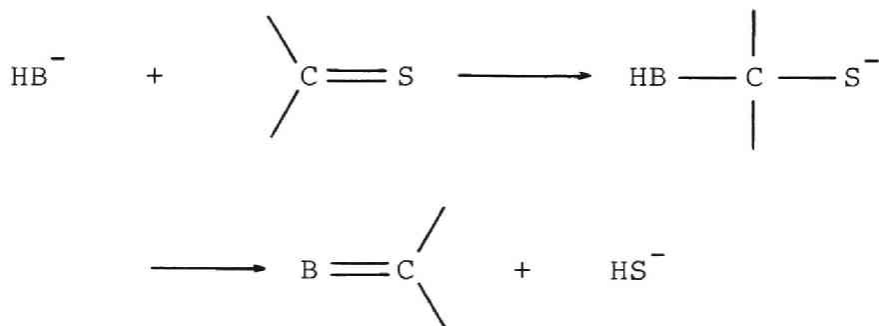


It is reasonable to expect that the larger electronegativity of oxygen (3.5) than that of sulfur (2.5)² will make the canonical form B more important when X is an oxygen than when it is a sulfur and the resonance energy would be larger for the carbonyl group than the thiocarbonyl group.



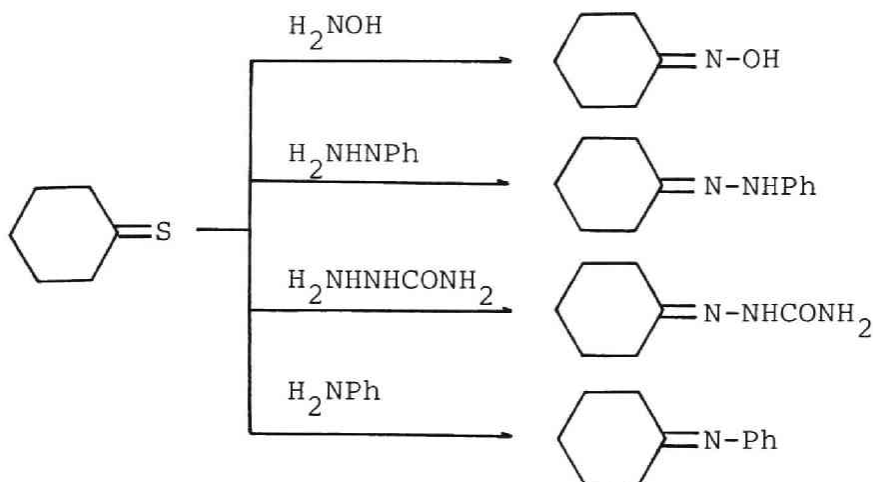
However, all of physical and chemical evidence invokes that B and C contribute more to the thiocarbonyl group than to the carbonyl group.

The general scheme for the reactions of thiocarbonyl compounds with nucleophiles may be formulated as shown in the following equation.³ In contrast to the carbonyl compounds, tetrahedral inter-

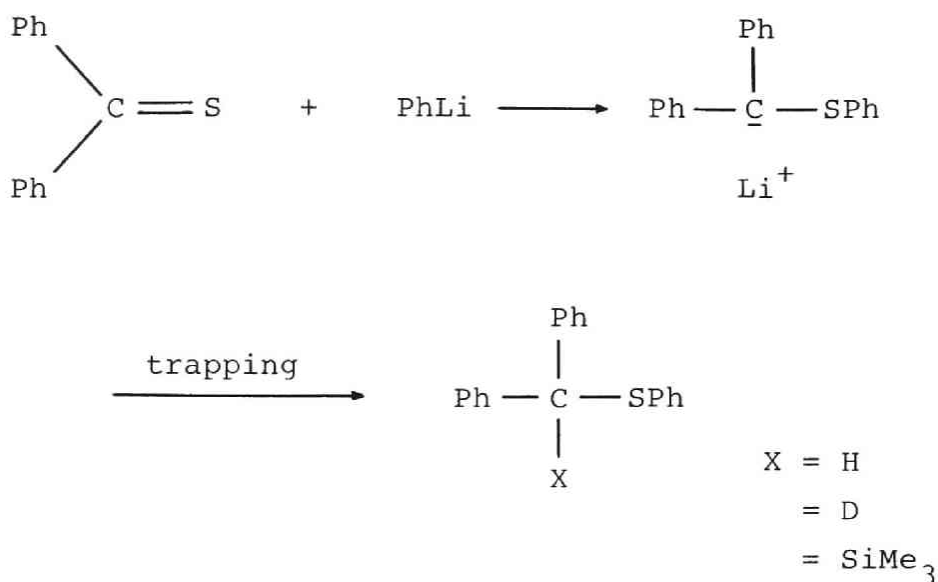


mediates⁴ are stable and have often been isolated. For example, thio-ketones react with hydrogen sulfide giving gem-dithiols at -40° and the reaction with ethanol affords ketals as final products, while the reaction with water yields ketones.

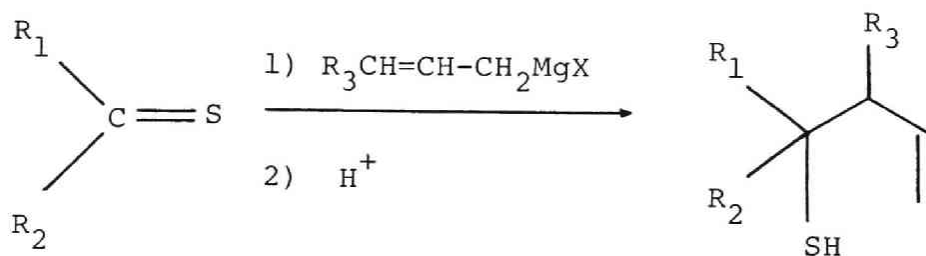
Cyclohexanethione, for example, reacts with carbonyl reagents without any catalyst,⁵ while reactions with carbonyl compounds generally require catalyses. As seen in the following scheme, typical nucleophiles attack at the carbon atom of thiocarbonyl group, which indicates that the large contribution of the canonical form (C^+-S^-) makes the thiocarbonyl group more reactive than the carbonyl group.



On the other hand, the Grignard reagents have often reported to attack at the sulfur atom of thiocarbonyl group, but not to the carbon atom. For example, Beak and Worley have studied the reactions of thiobenzophenone with a series of organometallic compounds,⁶ such as $PhMgBr$, $PhNa$, $BuLi$ and $PhLi$, and they concluded that these reactions in general proceed by the thiophilic addition mechanism, namely, the organometallic reagents initially attack at the sulfur atom of thiobenzophenone to give the intermediate adduct. From the trapping experiments, the possibility that thiobenzophenone and $PhLi$ react by initial addition to carbon atom to give the anion (S^-), which rearrange to the carbanion (C^-), was discounted.

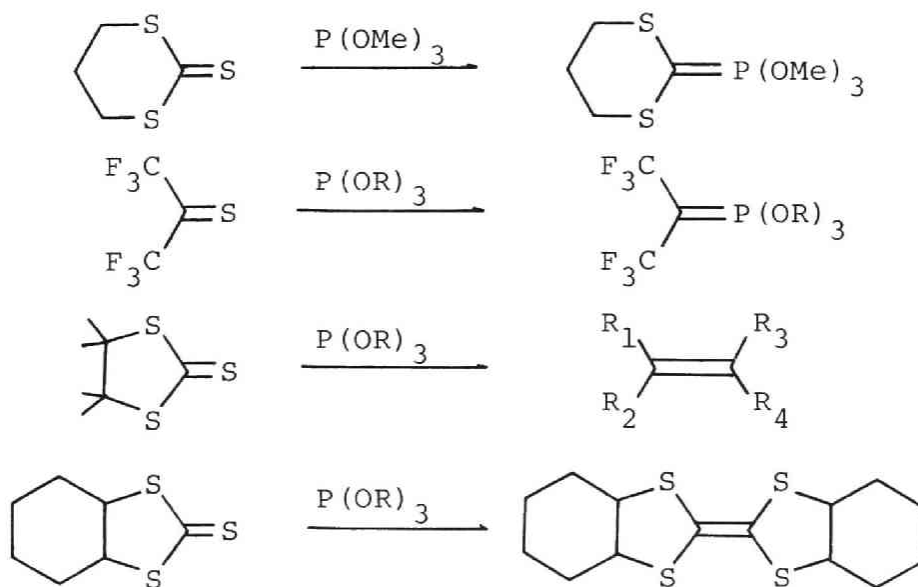


Different from the reactions above, thiobenzophenone, thio-pivalophenone, thiopinacolone, thiocamphor and thiofencone reacted with allylic Grignard reagents to form only C-alkylated products.⁷



Though the thiocarbonyl compounds have the interesting and peculiar reaction behavior, that is to say, they undergo two different reactions with nucleophiles (carbophilic attack and thiophilic attack), the studies on the chemistry of thiocarbonyl compounds are quite few in comparison with the chemistry of carbonyl compounds, and the applications for the organic synthetic reactions have scarcely been reported.

Trivalent organophosphorus compounds, such as phosphines and phosphites, are known to demonstrate both "carbophilicity" and "thiophilicity"⁸ toward organosulfur compounds. Therefore, the reactions of thiocarbonyl compounds with organophosphorus compounds have been the focus of interest in the chemistry of thiocarbonyl compounds. Though the reactions of trivalent phosphorus compounds with carbonyl compounds have often been reported, there are only few reports on the reactions of phosphites with thiocarbonyl compounds. For instance, phosphites reacted with 1,3-dithiacyclohexane-2-thione,⁹ hexafluoro-thioacetone,¹⁰ and thiofluorenone¹⁰ to afford the corresponding phosphoranes, and ethylenetrithiocarbonates also reacted with phosphites and gave olefins by desulfurization,^{11,12} in which reactions phosphites can be considered to attack at the sulfur atom of thiocarbonyl groups.



Those thiocarbonyl compounds employed in those works, however, were

aromatic thiones^{10,13} perfluorothione¹⁰ and cyclic trithiocarbonates, 9,11,12 and so the thiophilic attacks of phosphites are not always reflecting the reactivities of phosphites to the thiocarbonyl group.

In this thesis, the fundamental and systematic reactions of thiocarbonyl compounds with trivalent phosphorus compounds (phosphites and phosphine) are carried out and the new synthetic reactions are developed.

In chapter I, the reaction of cycloalkanethiones with trialkyl phosphites is described. As cycloalkanethiones are unstable, gem-dithiols are utilized as precursors and cycloalkanethiones are prepared by dehydrogen sulfide from gem-dithiols on heating. Cycloalkanethiones react with trialkyl phosphites to give 1-alkylthio- and/or 1-mercapto-cycloalkane phosphonic acid esters. This reaction is obviously explained by carbophilic attack of phosphites at the thiocarbonyl carbon atom to form betaine intermediate, and the following concerted migration mechanism of alkyl group and/or proton. These sulfur containing phosphonic acid esters are easily converted to cycloalkane phosphonic acid esters by Raney Ni treatment.

Chapter II deals with the reaction of dialkylthioketones with trialkyl phosphites. In this reaction, gem-dithiols are employed as precursors of thioketones and the phosphonic acid esters having alkylthio- and/or mercapto groups are obtained. This reaction is also interpreted in terms of carbophilic attack of phosphites. Especially, in the reaction of unsymmetrical thioketone, such carbophilic attacks occur to afford two absolute configurations (R- and S-), which are

detected by ^1H -nmr spectra.

Chapter III describes the new synthetic reactions of tetrathiafulvalene derivatives by the reaction of 4,5-electronegatively substituted (CN, COOMe, Ph)-1,3-dithiole-2-thiones with trivalent phosphorus compounds. These reactions are interpreted in terms of thiophilic attack of trivalent phosphorus compounds at the thiocarbonyl sulfur atom to afford phosphorane intermediate. From these tetrathiafulvalenes, new electronegatively substituted tetrathiafulvalenes and parent tetrathiafulvalene are prepared. These are very stable compared to the parent tetrathiafulvalene. In connection with this fact, chapter IV deals with the electronic structures and intramolecular charge-transfer absorption of tetracyanotetrathiafulvalene. The calculated results by ASMO-SCF-CI method, in which 3d-orbitals are taken into account, showed that the absorption band at the longest wave length is interpreted in terms of the intramolecular charge-transfer from the central electron rich tetrathioethylene part to the electron deficient dicyanoethylene part.

In chapter V, theoretical investigation of the reactions of thiocarbonyl compounds, aliphatic thioketones and 1,3-dithiole-2-thiones, by assuming two typical intermediates, namely, betaine and phosphorane, is carried out by the aids of CNDO/2 method. It is concluded that the reaction product is dependent on stability of the assumed intermediates.

Chapter VI deals with the reactions of dithioacetates and cyclopentenethione with trialkyl phosphites. Though trialkyl phosphites

generally behave as nucleophiles, in these reactions phosphites behave as base to abstract α -proton of thiocarbonyl group, and the bimolecular condensation products are obtained.

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CHAPTER I

REACTION OF CYCLOALKANETHIONES WITH TRIALKYL PHOSPHITES

— NEW SYNTHESSES OF CYCLOALKANE PHOSPHONIC ACID ESTERS^{*} —

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SUMMARY

Cycloalkanethiones were prepared from corresponding gem-cycloalkanedithiols by heating at the elevated temperature more than 80°. The resulting cycloalkanethiones reacted with trialkyl phosphites (trimethyl, triethyl and tri-iso-propyl phosphites) at 110 ° to give 1-alkylthio- and/or 1-mercapto-cycloalkane phosphonic acid esters, while triphenyl phosphite did not react with cycloalkanethiones even at elevated temperature. This reaction is obviously explained by carbophilic attack of phosphite at the thiocarbonyl carbon atom, and followed by the concerted migration mechanism via the resulting betaine intermediate. These sulfur containing phosphonic acid esters were easily converted to cycloalkane phosphonic acid esters by Raney Ni treatment in good yields.

INTRODUCTION

The chemistry of thiocarbonyl compounds¹ has attracted much attention owing to their interesting reactivities and preparative significance. Especially, the reactions of thiocarbonyl compounds with organophosphorus compounds have been the focus of interest in the past several years, because phosphites are known to demonstrate both "carbophilicity" and "thiophilicity"² toward organosulfur compounds. Carbonyl compounds are known to react with trivalent phosphorus compounds to give various products.³⁻⁷ For example, benzophenone reacts

with tri-iso-propyl phosphite to give tetraphenylethylene, tri-iso-propyl phosphate, propylene and di-iso-propyl benzhydryl phosphonate, where a mechanism involving betaine intermediates was postulated.⁸

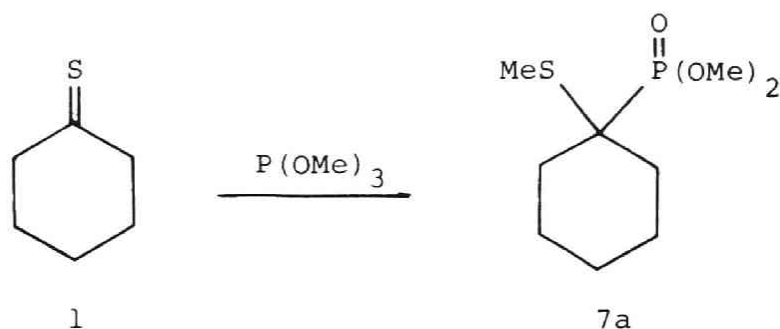
Although the reactions of trivalent phosphorus compounds with carbonyl compounds have been often reported, there are only a few reports on the reaction of trivalent phosphorus compounds with thiocarbonyl compounds which should be more reactive.^{9,10} For instance, Corey and Markl¹¹ reported the reaction of 1,3-dithiacyclohexane-2-thione with trimethyl phosphite to give 1,3-dithiacyclohexylidene phosphorane, which was converted to the phosphonic acid ester derivative by the rearrangement of methyl group.¹¹ Middleton and Scharkey also reported the reactions of hexafluorothioacetone and thiofluorenone with trialkyl phosphites to afford the corresponding phosphorane derivatives.¹² Thiocarbonyl compounds employed in those works were aromatic thiones,^{12,13} perfluorothione and cyclic trithiocarbonates.¹¹ All these reactions could be explained by initial thiophilic attack of phosphites at the thiocarbonyl sulfur atom.

In this chapter, cyclopentanethione, cyclohexanethione, cycloheptanethione and simple thiones were employed as thiocarbonyl compounds and reacted with trialkyl phosphites.

RESULTS AND DISCUSSION

The reaction of cyclohexanethione (1) with four equivalents of trimethyl phosphite in toluene at reflux temperature has been carried

out. Before heating the reaction mixture colored orange-pink, but the pink color gradually faded away as the reaction proceeded. After a complete fading of the pink color of 1, the work up of the reaction mixture afforded a 51 % yield of O,O-dimethyl-(1-methylthio)-cyclohexane phosphonic acid ester (7a). The structure of 7a was determined by its analytical and spectral data. The nmr and ir spectra charts



are illustrated in Fig.1. In the nmr spectrum of 7a, the protons of methyl group attached to the sulfur atom appeared as a singlet at δ 2.20 and those attached to the oxygen atom as a doublet at δ 3.86 with $J_{P-H}=10.1$ Hz. For comparison, the methyl resonances in cyclohexane phosphonic acid dimethyl ester, prepared from trimethyl phosphite and cyclohexyl bromide,¹⁴ appear as a doublet at δ 3.77 with $J_{P-H}=10.0$ Hz. The infrared spectrum of 7a revealed a strong band at 1240 and 1180 cm^{-1} which are characteristic of a P=O double bond and P-O-Me bond, respectively. Desulfurization of 7a with Raney Ni in ethanol afforded cyclohexane phosphonic acid dimethyl ester, which was identical with the authentic sample.

Thus, cyclohexanethione reacted with trimethyl phosphite to

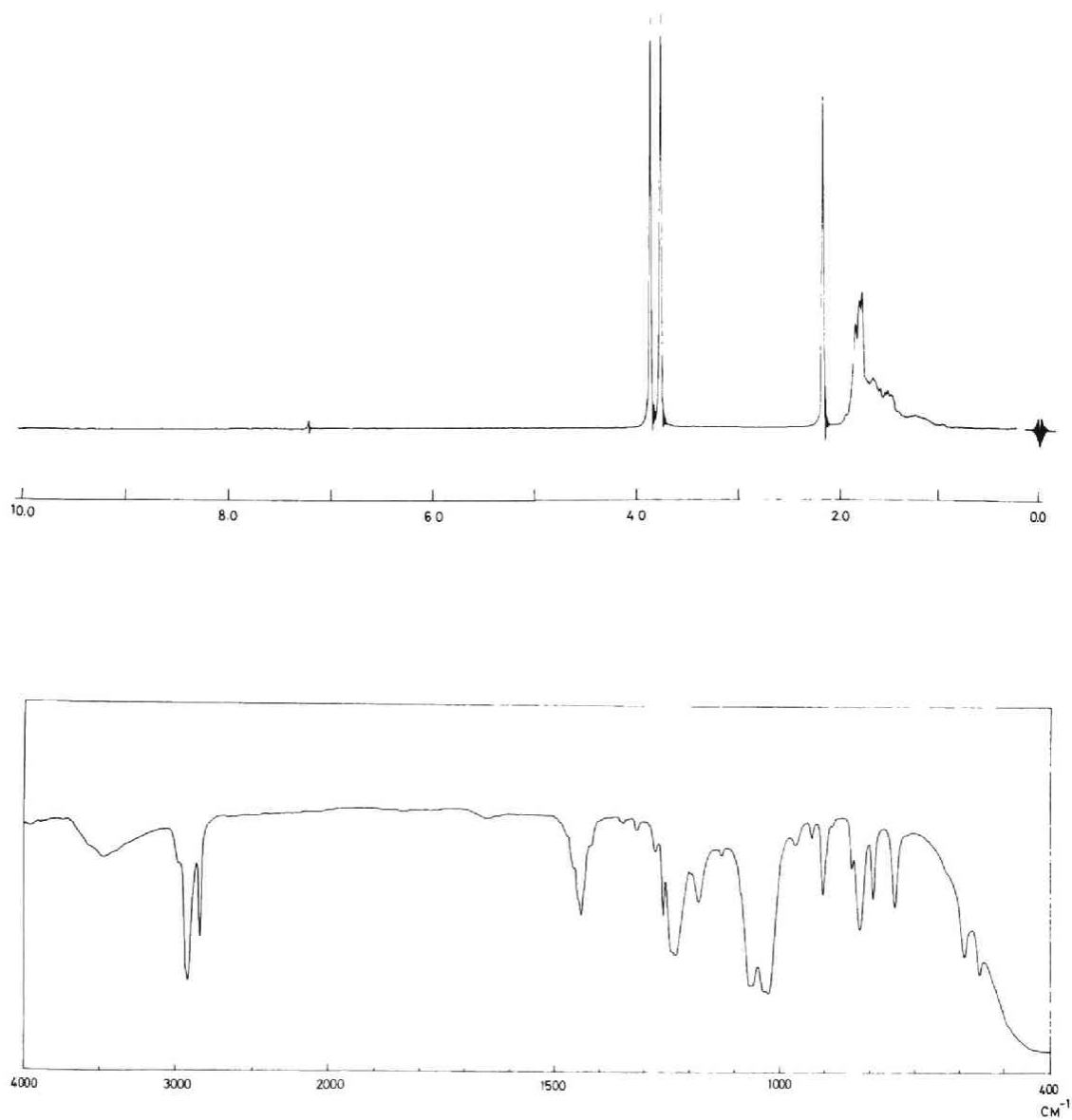
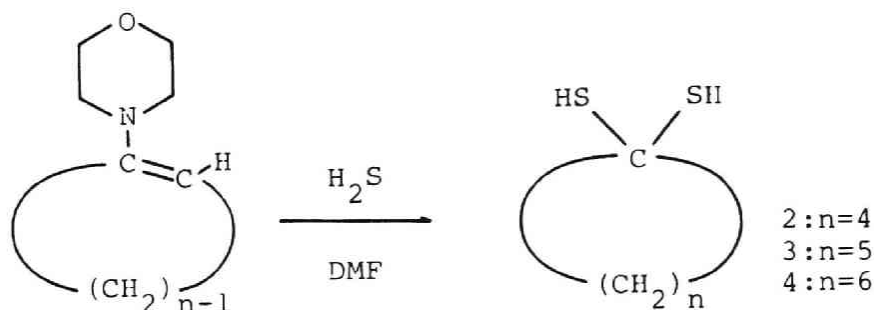


Fig. 1. ^1H -NMR and Infrared Spectra of O,O-Dimethyl-(1-methylthio)-cyclohexane Phosphonic Acid Ester (7a).

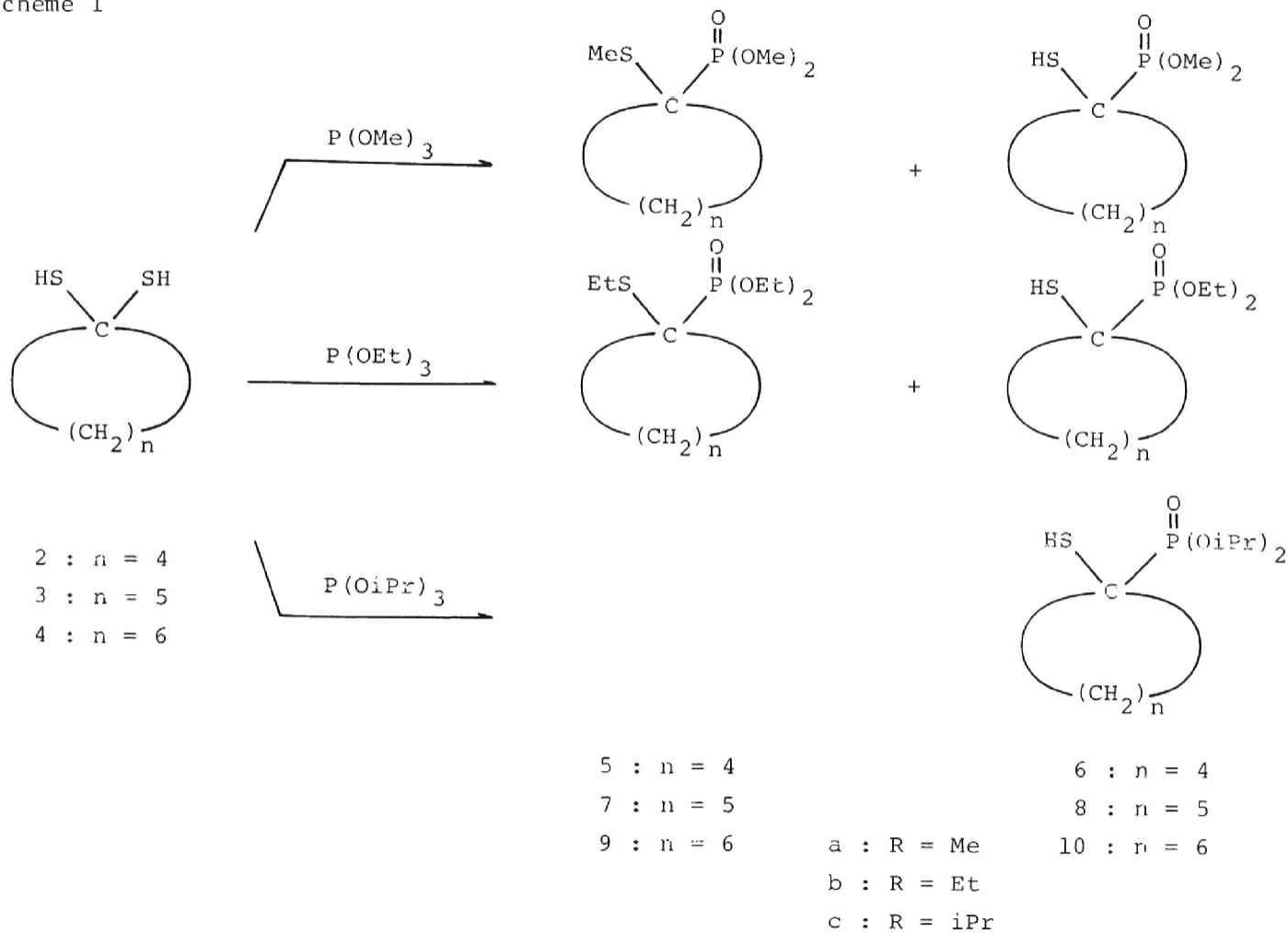
give phosphonic acid ester. However, it is generally known that the syntheses of thiones need strict conditions¹⁵ and aliphatic thiocarbonyl compounds are unstable and easily polymerize at room temperature.¹⁶ For these difficulties in handling, gem-cycloalkanedithiols (2-4) were employed as precursors of cycloalkanethiones, since heating of cyclohexanedithiol, as example, is known to afford cyclohexanethione by elimination of hydrogen sulfide.¹⁷ These cycloalkanedithiols were easily prepared from corresponding 1-morpholino-cycloalkenes and hydrogen sulfide in N,N-dimethylformamide.¹⁸ Thus, in



this study gem-dithiols were used in most cases as starting materials, because they are more available than cycloalkanethiones.

Reaction of cyclopentanethione. When a solution of cyclopentanedithiol (2) and four equivalents of trimethyl phosphite in toluene was heated to reflux temperature under nitrogen atmosphere, hydrogen sulfide evolved and the color of the reaction mixture turned to pink. The evolution of hydrogen sulfide was detected by introducing the stream of nitrogen into an aq. solution of CuSO_4 . The evolution of hydrogen sulfide and the pink coloration indicate the formation of cyclopentanethione in the reaction. After the subsequent decolori-

Scheme I



zation was complete, distillation of the reaction mixture gave 0,0-dimethyl-(1-methylthio)-cyclopentane phosphonic acid ester (5a) in 56 % yield. The structure of 5a was determined by its spectral data. In the nmr spectrum, the protons of methyl group attached to the sulfur atom appeared as a singlet at δ 2.23 and those attached to the oxygen atom as a doublet at δ 3.85 with $J=11.0$ Hz. The infrared spectrum revealed a strong band at 1240 cm^{-1} which is characteristic of a P=O double bond.

The reaction of 2 with triethyl phosphite gave a mixture of two sulfur containing phosphonic acid esters, which were distilled as a mixture and separated and analysed by gas chromatography. The second fraction was 0,0-diethyl-(1-ethylthio)-cyclopentane phosphonic acid ester (5b). The structures were determined by the elemental analyses and spectral data. The nmr spectrum of 5b consisted of a quartet at δ 2.86(2H, $J=7.5\text{Hz}$, SCH_2CH_3), double of quartets at δ 4.08 and 4.16(4H, $J_{\text{H-H}}=7.5\text{Hz}$, $J_{\text{P-H}}=8.5\text{Hz}$, POCH_2CH_3) and two triplets at δ 1.20(3H, $J=7.5\text{Hz}$, SCH_2CH_3) and 1.32(6H, $J=7.5\text{Hz}$, POCH_2CH_3). The infrared spectrum revealed an absorption at 1235 cm^{-1} characteristic of a P=O double bond. These spectral features are totally consistent with the assignment of 5b. On the other hand, the first fraction was 0,0-diethyl-(1-mercapto)-cyclopentane phosphonic acid ester (6b). In the nmr spectrum of 6b, the resonances of ethyl group attached to the sulfur atom disappeared, and the mercapto proton appeared as a doublet at δ 2.24, the methylene protons as double quartets at δ 4.11 and 4.19, and the methyl protons as a triplet at δ 1.34 with $J_{\text{H-H}}=7.1\text{Hz}$.

and $J_{P-H}=8.5\text{Hz}$, respectively. The infrared spectrum of 6b exhibited an absorption at 2505 cm^{-1} assigned to the SH stretching but the absorption was not so strong probably owing to the hydrogen bonding between SH and P=O groups.

The reaction of 2 with tri-iso-propyl phosphite gave only 0,0-di-iso-propyl-(1-mercapto)-cyclopentane phosphonic acid ester (6c) in good yield (83%), but no ester having an alkylthio group was obtained. Similarly to 6b, in the nmr spectrum the mercapto proton appeared at δ 2.28 and in the infrared spectrum a weak band at 2510 cm^{-1} assigned to SH group. In the reactions giving mercapto phosphonic acid esters (6b and 6c), the formation of olefins was detected by introducing the stream of nitrogen, after passing the alkali tube, into the carbon tetrachloride solution of bromine, when the color of the solution disappeared.

Reaction of cyclohexanethione. To a solution of cyclohexanedithiol (3) in toluene was added four equivalents of trimethyl phosphite with stirring under nitrogen. As the reaction mixture was elevated to the reflux temperature, the evolution of hydrogen sulfide and the change of the color of the solution to pink were observed. After the pink color disappeared completely, distillation gave 0,0-dimethyl-(1-methylthio)-cyclohexane phosphonic acid ester (7a) in 70 % yield. The structure was assigned on the basis of the analytical and spectral data, and was confirmed by comparing the spectral data of the product (7a) to those prepared from cyclohexanethione (1).

Reaction of 3 with triethyl phosphite was carried out in the

same reaction condition gave 0,0-diethyl-(1-ethylthio)-cyclohexane phosphonic acid ester (7b) and 0,0-diethyl-(1-mercapto)-cyclohexane phosphonic acid ester (8b) in 20% and 30% yields, respectively, which were obtained as a mixture by distillation and separated by gas chromatography. These structures were determined by their spectral data as the case of the reaction of 2. The nmr spectrum of 7b consisted of two kinds of ethyl groups (one SCH_2CH_3 and two OCH_2CH_3 's) and the infrared spectrum revealed an absorption at 1240 cm^{-1} . In the nmr spectrum of 8b, the mercapto proton appeared at $\delta\ 1.93$. The infrared spectrum of 8b clearly exhibited an absorption at 2500 cm^{-1} assigned to the SH group.

A similar reaction of 3 with tri-iso-propyl phosphite gave only one product, 0,0-di-iso-propyl-(1-mercapto)-cyclohexane phosphonic acid ester (8c), in 81 % yield. This product showed the SH absorption band in the infrared spectrum and the signal at $\delta\ 1.91$ in the nmr spectrum, which clearly supported the structure of 8c. The formation of alkylthio-type product was not found.

Triphenyl phosphite did not react with 3 in toluene at reflux temperature for 24 hr, and 3 turned to trithiane.

Reaction of cycloheptanethione. A solution of cycloheptanedithiol (4) and four equivalent trimethyl phosphite in toluene was refluxed and the evolution of hydrogen sulfide and the coloration to pink were observed. After the complete decolorization, though it needed more than 48 hr probably because of the slow formation of thione by dehydrogen sulfide of 4, distillation afforded 0,0-dimethyl-(1-methyl-

thio)-cycloheptane phosphonic acid ester (9a) in 48 % yield, whose structure was determined by the nmr and infrared spectra, a singlet signal at δ 2.21 and a strong band at 1240 cm^{-1} , respectively.

The reaction of 4 with triethyl phosphite gave a mixture of two esters, O,O-diethyl-(1-ethylthio)-cycloheptane phosphonic acid ester (9b) and O,O-diethyl-(1-mercapto)-cycloheptane phosphonic acid ester (10b), in 23% and 21% yields, respectively, which were obtained as a mixture by distillation and separated by gas chromatography, too. Their structures were determined by nmr spectral data similar to the cases mentioned above. The nmr spectrum of 9b consisted of two kinds of ethyl groups (SCH_2CH_3 and OCH_2CH_3) and in the nmr spectrum of 10b the mercapto proton appeared at δ 2.25.

The reaction of 4 with tri-iso-propyl phosphite gave only O,O-di-iso-propyl-(1-mercapto)-cycloheptane phosphonic acid ester (10c) in 76 % yield. According to the SH absorption band at 2500 cm^{-1} in the infrared spectrum and the signal attributable to SH appeared at δ 2.11 in the nmr spectrum, the structure of 10c was supported.

These results are summarized in Scheme I and in Table 1. As seen in Table 1, the reactions proceeded rather slowly in benzene, toluene and xylene, though the use of such solvents makes the work-up of the reaction mixture easier owing to the absence of side reactions. By addition of small amount of ethanol or isobutanol to the reaction, the reaction of 3 with trimethyl phosphite was quite accelerated to give 7a together with trace of O,O-dimethyl-(1-mercapto)-cyclohexane phosphonic acid ester (8a). However, when ethanol itself

Table 1. Reaction Conditions and Yields of Products in the Reaction of
Cycloalkanedithiols with Trialkyl Phosphites

Substrates (gem-dithiols)	Reactants (phosphites)	Reaction Time (hr)	Solvents	Yield (%)	
				alkylthio	mercapto
cyclopentane	P(OMe) ₃	10	toluene	56	0
dithiol (2)	P(OEt) ₃	12	toluene	20 [*]	26 [*]
	P(OiPr) ₃	10	toluene	0	83
cyclohexane	P(OMe) ₃	20	benzene	59	0
dithiol (3)		20	toluene	70	0
		10	xylene	68	0
		5	toluene	63	trace
			(ethanol)		
		5	ethanol	23	39 ^{**}
		5	i-butanol	24	40
		5	acetonitrile	37	34

Table 1. (continued)

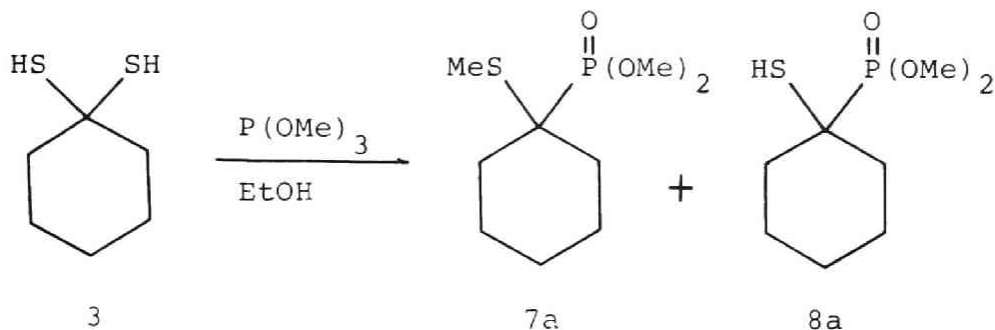
Substrates (gem-dithiols)	Reactants (phosphites)	Reaction Time (hr)	Solvents	Yield (%)	
				alkylthio	mercapto
cyclohexane	P(OMe) ₃	5	propionitrile	29	36
dithiol (3)		7	dioxane	63	trace
	P(OEt) ₃	20	toluene	20*	30*
	P(OiPr) ₃	20	toluene	0	89
		5	ethanol	0	85
	P(OCr) ₃ ***	20	toluene	65	0
cycloheptane	P(OMe) ₃	48	toluene	48	0
dithiol (4)	P(OEt) ₃	40	toluene	23*	21*
	P(OiPr) ₃	48	toluene	0	76

*: determined by gas chromatography

**: 7.6% of ethyl ester was contained.

***: Cr = $-\text{CH}_2-\text{CH}=\text{CHCH}_3$

was used as a solvent, 8a was obtained in fair yield. And when other

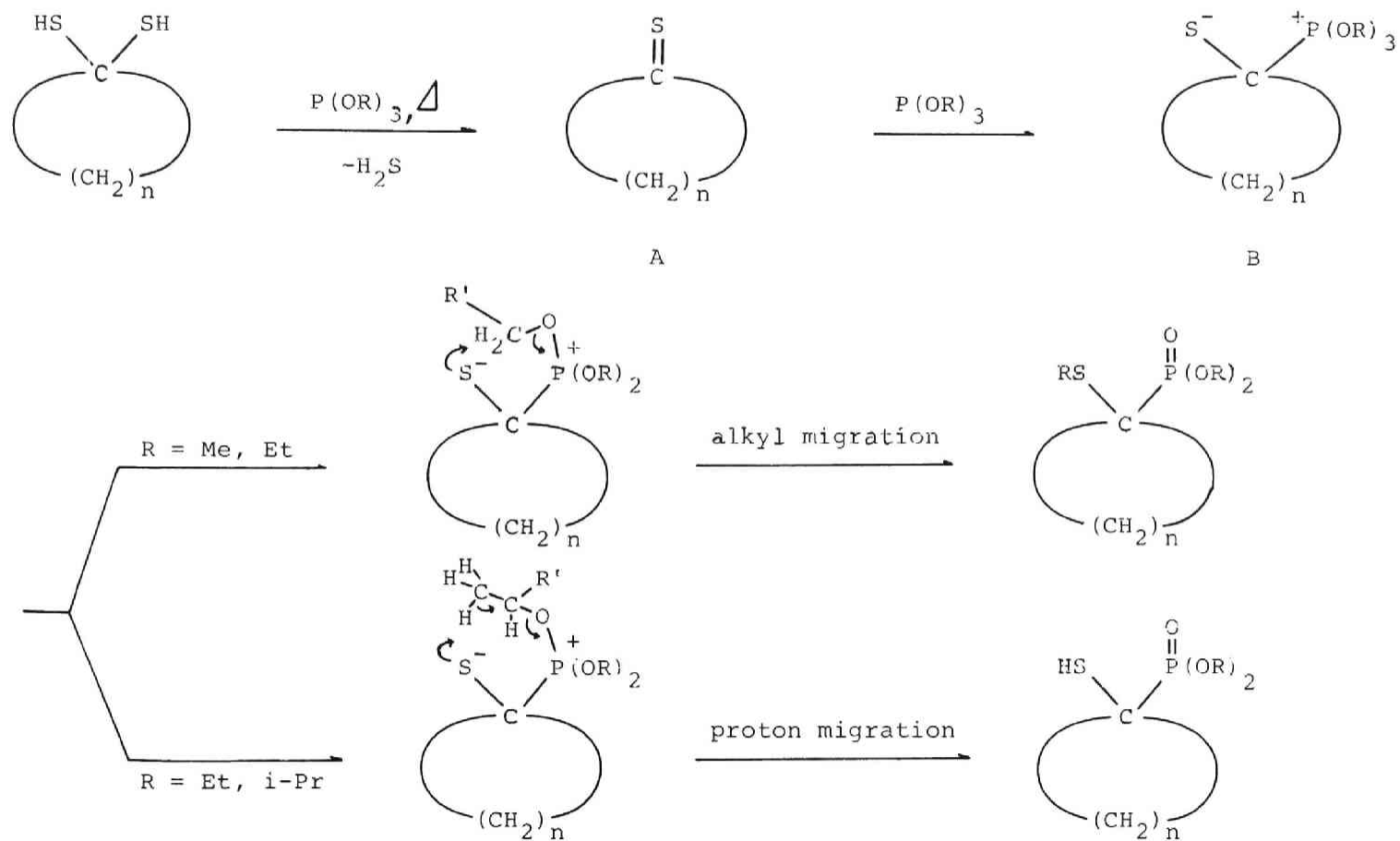


polar solvents, such as isobutanol, acetonitrile, propionitrile and dioxane, were used as solvents, the reaction proceeded more rapidly than toluene was used. But when the solvents having an active hydrogen were used, 8a was also obtained in considerable yields.

The mechanistic interpretation of the reactions of cycloalkanethiones (cycloalkanedithiols) with trialkyl phosphites is outlined in Scheme II. The reaction would be initiated by removal of hydrogen sulfide from cycloalkanedithiols and form the corresponding thiones, which might be accelerated by trialkyl phosphites owing to the action as base. As an evidence, in the reaction of cyclohexanedithiol with triphenyl phosphite, the evolution of hydrogen sulfide was observed at the initial reaction time and the pink color of the solution gradually disappeared with the elapse of time and the trithiane was obtained, which obviously indicate the formation of cyclohexanethione.

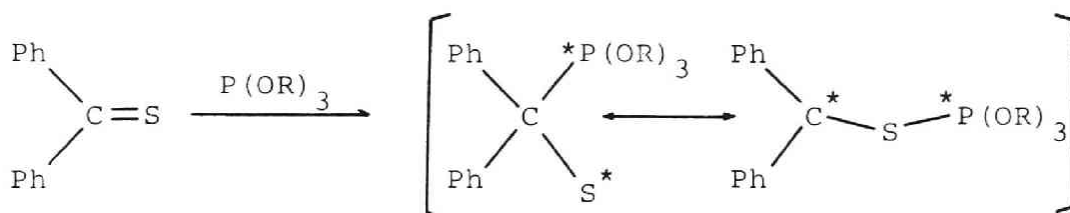
The resulting cycloalkanethiones (A) might immediately react with excess trialkyl phosphites. Though trialkylphosphites are known to behave as thiophilic reagents toward thiocarbonyl groups, in this reaction the phosphorus atom of phosphite seems to attack directly at

Scheme II



the carbon atom of thiocarbonyl group. This carbophilic attack of trialkyl phosphite would form the betaine intermediate (B), but not phosphorane via attack at the sulfur atom of thiocarbonyl group. Addition of small amount of polar solvent such as ethanol would stabilize the betaine intermediate (B) and so make the reaction proceed more rapid.

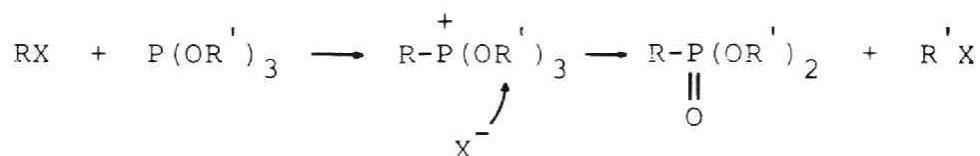
In the reaction of thiobenzophenone with trialkyl phosphites, Ogata et al. suggested a reaction intermediate similar to this betaine intermediate B.¹³ The intermediate, they suggested, is not a



zwitter-ion(betaine), but a biradical, since the migration of alkyl carbonium ions^{11,12} in an ionic intermediate such as that of Arbusov reaction¹⁹ was not observed. In this experiment, however, the intermediate should be a zwitter-ion type(B), because the migration of alkyl group occurred.

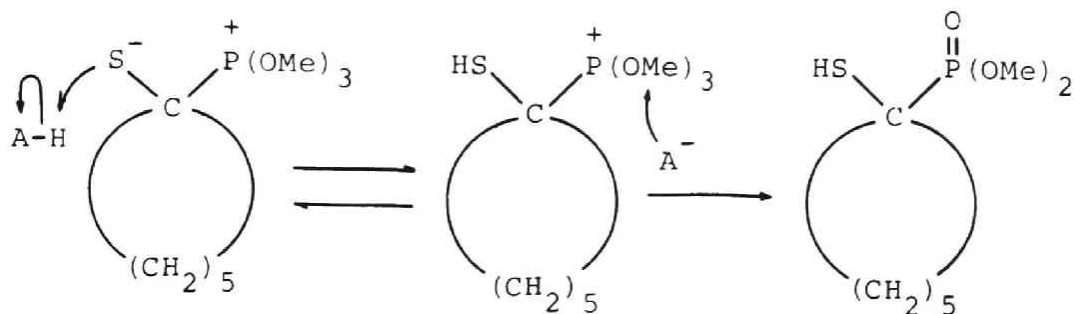
From the intermediate B the migration of alkyl group or proton would afford the phosphonic acid esters containing a sulfur atom as alkylthio or mercapto group. When phosphites were trimethyl and/or triethyl phosphites, the negatively charged sulfur atom of the betaine intermediate B would intramolecularly interact with alkyl groups from back side and result in the formation of phosphonic acid esters bear-

ing sulfur atom as an alkylthio group. This migration is very similar to that of the Arbusov reaction, in which halide anion is well known to attack at alkyl group from backside and result in the formation of alkyl halide and phosphonic acid esters. However, when tri-



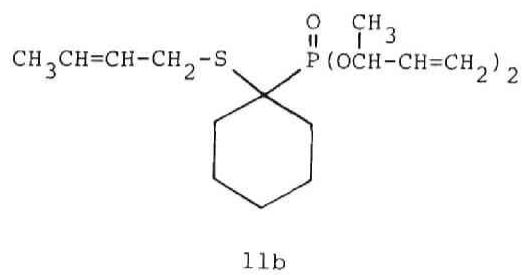
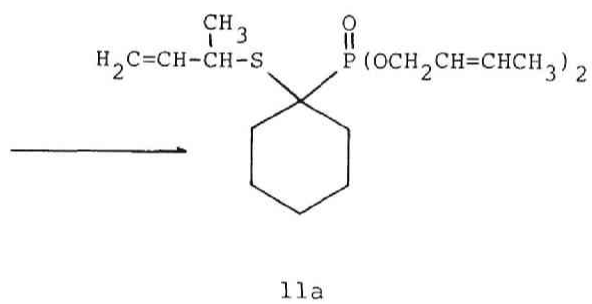
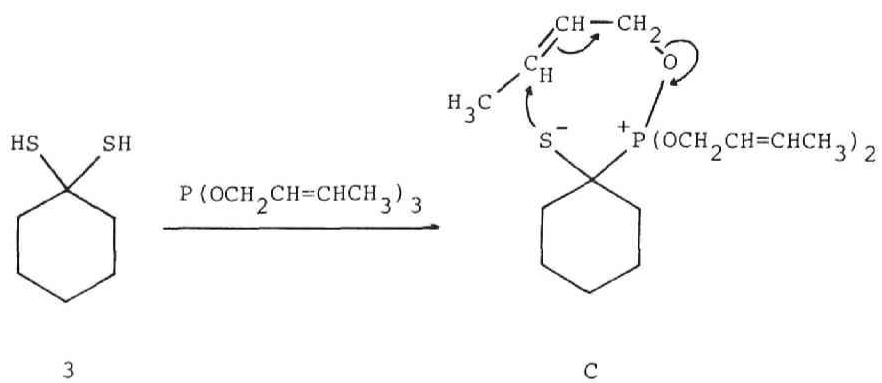
ethyl and/or tri-iso-propyl phosphites were employed, these backside attack of negatively charged sulfur atom of the betaine intermediate B should be hindered by methyl groups, and therefore the proton migration would take place via a cyclic concerted mechanism. In those proton migration a stepwise mechanism involving the generation of carbonium ions also might be excluded for the following reason: (1) In nonpolar solvents, such as benzene, toluene and xylene, those formation of carbonium ions would unlikely take place. (2) In spite of the order of increasing stability of carbonium ions ($\text{Me}^+ < \text{Et}^+ < \text{i-Pr}^+$), the product ratios of alkylthio to mercapto phosphonic acid esters decrease in this series. When the polar solvents, excepted dioxane, were employed in this reaction with trimethyl phosphite, the favorable formation of 8a might possibly be explained by the following reaction scheme. The betaine intermediate B would abstract the acidic proton of solvents in equilibrium, and the interaction of resulting intermediate (C) with solvent anions would afford mercapto phosphonic acid ester 8a. However, the solvent interacted products, Me-A, could

not be detected. And the fact that in dioxane the reaction of 3 with trimethyl phosphite gave only one product, 7a, would support this reaction mechanism.



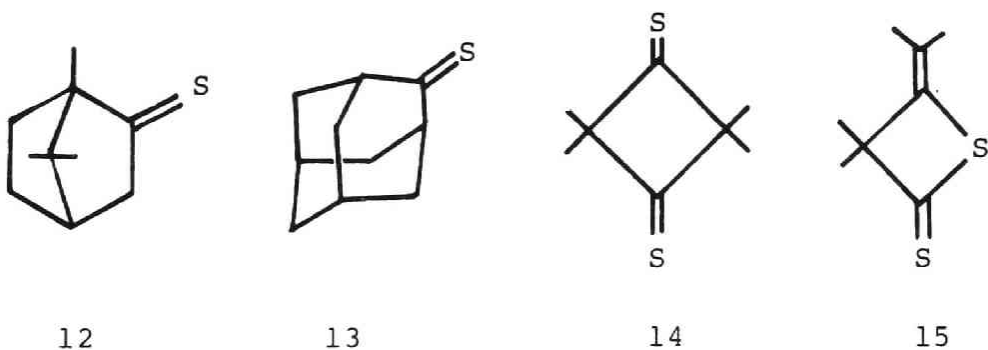
In connection with the study of whether the migration took place via concerted or stepwise mechanism, the reaction of 3 with tricrotyl phosphite was carried out. As shown in Scheme III, the phosphite attacked at the carbon atom of thiocarbonyl group and form the betaine intermediate (D). If the migration occurs stepwise, as the crotyl carbonium ion is known to be stable, the products must be the mercapto type phosphonic acid ester and/or the mixture of crotylthio and methylallylthio phosphonic acid esters. The product obtained in 65% yield by distillation was assigned to be the alkylthio-type phosphonic acid ester on the basis of the analytical data. The infrared spectrum showed an absorption at 910 cm^{-1} attributable to the terminal vinyl group, and the nmr spectrum exhibited a quartet at δ 4.33(1H, $J=7.5\text{Hz}$, $\text{SCH}-\text{CH}_3$) and a doublet at δ 1.27-1.47(3H, $J=7.5\text{Hz}$, $\text{SCH}-\text{CH}_3$), which mean clearly that the alkyl group attached to the sulfur

Scheme III



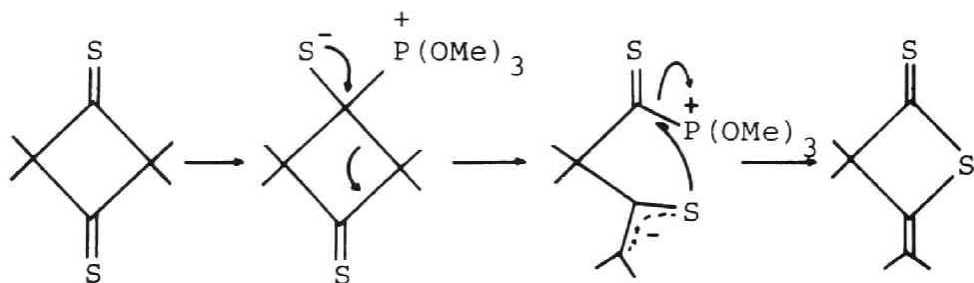
atom is not crotyl ($-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$) but methylallyl ($-\text{CH}(\text{CH}_3)-\text{CH}=\text{CH}_2$). Furthermore, the reaction of 3 with trimethylallyl phosphite was also examined. As expected from the result mentioned above, only one kind of alkylthio-type phosphonic acid ester (11b) was obtained. In the nmr spectrum of 11b the methylene protons appeared as a doublet at δ 3.36 (2H, $J=7.0\text{Hz}$, $\text{S}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$), which means that alkyl group attached to the sulfur atom is not methylallyl but crotyl. Therefore, it is reasonably considered that the migration took place via cyclic concerted mechanism. That is to say, the attack of the negatively charged sulfur atom occurred on the carbon atom of carbon-carbon double bond, just as in the thio-Claisen rearrangement, not directly on the carbon atom adjacent to the oxygen.

Reactions of other cycloalkanethiones. Though the reactions of other cycloalkanethiones, such as thiocamphor (12), adamantanethione (13) and 2,2,4,4-tetramethylcyclobutane-1,3-dithione (14), with trimethyl phosphite were carried out, the expected reaction did not occur. In



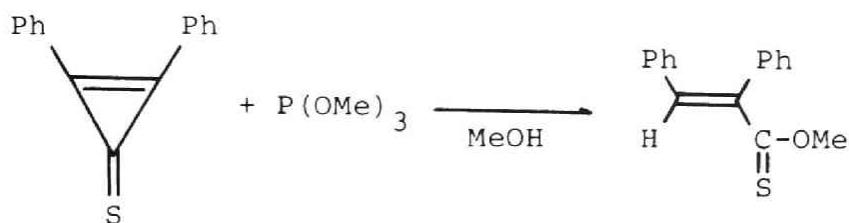
the case of the former two thiones, 12 and 13, this resistance to the expected reaction is reasonably explained by steric hindrance to attack of phosphite, that is to say, the bulkiness of two methyl groups

for 12 and of four methylenes for 13. The reaction of 14 with trimethylphosphite gave the dithiolactone(15) quantitatively, which is different from the result of the reaction of tetramethyl cyclobutanedione with trimethyl phosphite,²⁰ in which reaction the phosphonic acid esters were obtained. The formation of 15 from 14 is explained by the following reaction scheme. First, the trimethyl phosphite



would similarly attack at the thiocarbonyl carbon atom and form the betaine intermediate. However, the ring opening reaction would be preferred to the migration of alkyl group. Further, the recyclization reaction from the resulting intermediate would afford the dithiolactone and trimethyl phosphite.

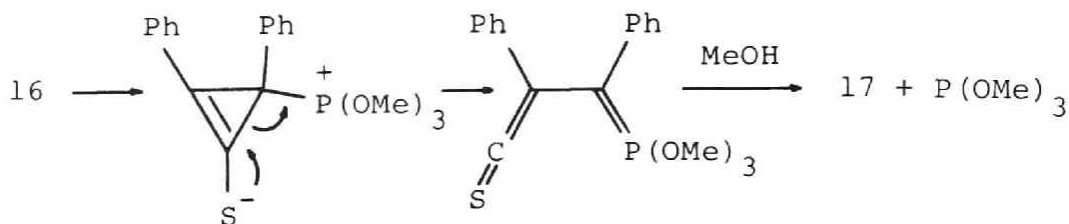
Reaction of cyclopropenethione. In the view of cyclic thione, the reaction of diphenylcyclopropenethione (16) with trimethyl phosphite was carried out. To a solution of 16 in toluene was added dropwise equivalent trimethyl phosphite at 0° with stirring under nitrogen. The color of the solution gradually turned to dark red from light yellow. After 30 min. a small amount of methanol was added and the reaction mixture was elevated to room temperature and allowed to stand for 1 hour. In the time the solution turned to orange and the work-up by column chromatography on silica afforded methyl α -phenyl-trans-



thiocinnamate (17) in 89 % yield, whose structure was assigned on the basis of analytical and spectral data.

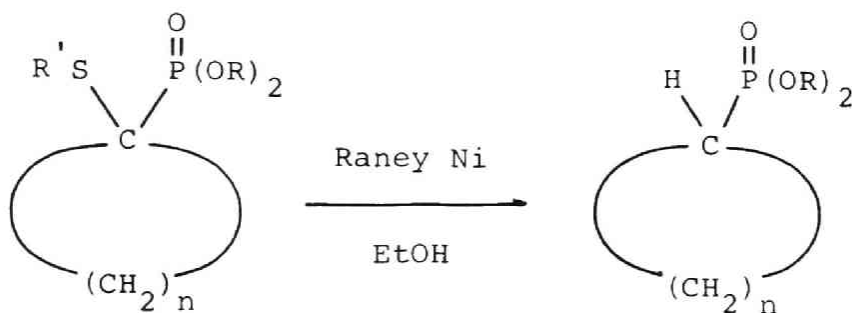
The mechanistic interpretation of this reaction is outlined in Scheme IV. The reaction should be initiated by the attack of trimethyl phosphite not at the carbon atom of thiocarbonyl, but at the carbon atom of olefin just as the Michael addition. The resulting zwitter-ion intermediate would undergo the ring opening to form thio-ketene phosphorane. In general thioketenes are known to be very reactive toward alcohols and amines to give thioesters and thioamides, respectively.²¹ On the other hand, the thioketene phosphorane intermediate unlike usual ylide did not react with benzophenone.²² These facts indicate that the nucleophilic attack of methanol takes place preferentially on the thioketene group rather than the phosphorane group. The reaction would proceed through the concerted pathway involving facile elimination of trimethyl phosphite as seen in Scheme IV. Similar ketene phosphorane intermediate and reaction mechanism were suggested by Takamizawa et al. in the reaction of diphenylcyclopropenone with triethyl and trimethyl phosphites.²³ But when di-*t*-butylthiocyclopropenethione was employed as thiocarbonyl compounds, such ring opening did not occur and the migration of methyl group in

the betaine-type intermediate gave cyclopropene phosphonic acid ester in good yield.²⁴



Syntheses of cycloalkane phosphonic acid esters by Raney Ni reduction.

All these phosphonic acid esters are new type of esters in the view of bearing sulfur as alkylthio or mercapto groups. These sulfur containing phosphonic acid esters were easily converted to cycloalkane phosphonic acid esters in good yields by Raney Ni reduction in ethanol under reflux for 10-20 hr. The results are summarized



in Table 2. In the case of diethyl phosphonic acid esters, the mixture of two type esters was directly used. The overall yields from gem-dithiols did not vary whether sulfur containing esters were isolated before reduction or the reaction mixtures were directly used.

In general, the phosphonic acid esters have been prepared from alkyl halides and trialkyl phosphites by the Arbusov reaction so far,

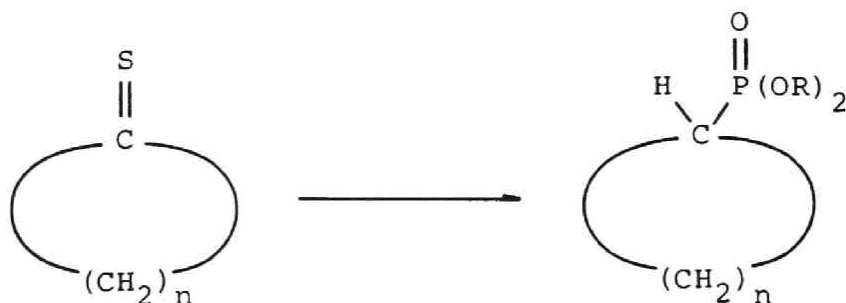
Table 2. Yields of Cycloalkane Phosphonic Acid Esters by
Desulfurization of 1-Alkylthio- and 1-Mercapto-
Cycloalkane Phosphonic Acid Esters with Raney Ni.

Substrates	Products	Yield %	(Yield %) *
5a	18a	82	(46)
5b + 6b **	18b	79	(37)
6c	18c	89	(74)
7a	19a	78	(55)
7b + 8b **	19b	92	(46)
8c	19c	82	(73)
9a	20a	84	(41)
9b + 10b **	20b	80	(33)
10c	20c	82	(63)

*: numbers in the parenthesis indicate the overall
yield of cycloalkane phosphonic acid esters from
gem-dithiols.

** : mixtures of ethyl esters (having ethylthio and
mercapto group) were directly used.

but the yields of cycloalkane phosphonic acid esters are known to be quite low because of the undesirable side reactions, as example the removal of hydrogen halide from alkyl halides, especially in the use of secondary alkyl halides.²⁵ In this reaction, such side reaction was not observed and phosphonic acid esters were obtained in good yields as shown in Table 2. Thus cycloalkane phosphonic acid esters can be easily synthesized from thiones.



EXPERIMENTAL

The infrared spectra were recorded on a Hitachi EPI-G3 grating infrared spectrophotometer, the nmr spectra were recorded on a Varian Associate AH-100 spectrometer. The chemical shifts are given in ppm relative to the internal TMS. Mass spectra were taken on a Hitachi RMU-6C mass spectrometer. Elemental analyses were carried out at the Elemental Analytical Center of Kyoto University. Gas-liquid chromatography was carried out with a Shimazu gas chromatograph Model GC-6A, using the stainless steel column packed with 20% silicon DC-550 on celite 545.

Materials. Cyclohexanethione was prepared as described by Mayer et

al..²⁶ Cyclohexanedithiol and cyclopentanedithiol were prepared from 1-morpholino-cyclohexene and -cyclopentene according to the literature of Djerassi and Tursch.¹⁸ Cycloheptanedithiol was similarly prepared from 1-morpholino-cycloheptene with hydrogen sulfide in 73 % yield (62-63°C, 2.0 mmHg). Thiocamphor,²⁷ adamantanethione²⁸ and 2,2,4,4-tetramethyl-cyclobutane-1,3-dithione²⁹ were prepared according to the reported methods. Diphenylcyclopropenethione was prepared from diphenylcyclopropenone³⁰ with hydrogen chloride and sulfide in ethanol as reported.³¹ Trimethyl phosphite and triethyl phosphite were commercial materials and were used after distillation. Tri-iso-propyl and tricrotyl phosphites were prepared utilizing the procedure of Ford-Moore and Jerry³² from phosphorus trichloride and the corresponding alcohols, bp 60-61°C(10 mmHg) and 104-105°C(2.5 mmHg), respectively.

Reaction of Cyclohexanethione with Trimethyl Phosphite. A mixture of cyclohexanethione (1.14g) and trimethyl phosphite (5.0g, 4 equivalent) in 30 ml of toluene was heated at reflux temperature under nitrogen overnight, producing colorless solution. After removal of toluene and excess trimethyl phosphite, the oily residue was distilled to give 1.21g (57%) of 7a as a colorless liquid, bp 112-113°C(2.5 mmHg); ir (neat) 1230(P=O), 1180 and 1040 cm^{-1} ; nmr (CDCl_3) δ 1.45-1.95(m, 10H, $-(\text{CH}_2)_5-$), 2.20(s, 3H, SCH_3) and 3.86(d, 6H, $J=10.1\text{Hz}$, P-O-CH_3); mass spectrum m/e 238(M^+).

Anal. Calcd for $\text{C}_9\text{H}_{19}\text{O}_3\text{PS}$: C, 45.37; H, 8.04; P, 13.00.

Found: C, 45.08; H, 8.38; P, 13.38.

General Procedure for Reaction of the Cycloalkanedithiols (2-4) with Trialkyl Phosphites. A mixture of 0.01 mole of cycloalkanedithiol (2-4) and 0.04 mole of trialkyl phosphite in 30 ml of toluene was heated at reflux temperature under nitrogen for 20-50 hr. After removal of toluene and excess trialkyl phosphite, the residue was distilled under vacuum to give colorless viscous liquid. In the reactions with triethyl phosphite, the distillates were mixtures of 1-ethylthio- and 1-mercapto-cycloalkane phosphonic acid esters, which were separated by gas chromatography and yields were determined.

The boiling points and ir, nmr and mass spectral data and the results of elemental analyses are as following:

O,O-Dimethyl-(1-methylthio)-cyclopentane phosphonic acid ester (5a): bp 103-104°C(4.0mmHg); yield 56%; ir (neat) 1240(P=O), 1180 and 1040 cm^{-1} ; nmr (CDCl_3) δ 1.47-2.26(m, 8H, $-(\text{CH}_2)_4-$), 2.23(s, 3H, SCH_3) and 3.85(d, 6H, $J=11.0\text{Hz}$, P-O-CH_3); mass spectrum m/e 224(M^+).

Anal. Calcd for $\text{C}_8\text{H}_{17}\text{O}_3\text{PS}$: C, 42.85; H, 7.64; P, 13.81.

Found: C, 42.95; H, 7.84; P, 13.57.

O,O-Diethyl-(1-ethylthio)-cyclopentane phosphonic acid ester (5b): bp 102-103°C(2.5 mmHg) as a mixture of 5b and 6b; yield 20%; ir (neat) 1235(P=O), 1162 and 1030 cm^{-1} ; nmr (CDCl_3) δ 1.20(t, 3H, $J=7.5\text{Hz}$, $\text{S-CH}_2\text{CH}_3$), 1.32(t, 6H, $J=7.2\text{Hz}$, $\text{P-O-CH}_2\text{CH}_3$), 1.5-2.2(m, 8H, $-(\text{CH}_2)_4-$), 2.86(q, 2H, $J=7.5\text{Hz}$, $\text{S-CH}_2\text{CH}_3$) and 4.08 and 4.17(double q, 4H, $J_{\text{H-H}}=7.2\text{Hz}$, $J_{\text{P-H}}=8.5\text{Hz}$, $\text{P-O-CH}_2\text{CH}_3$); mass spectrum m/e 266(M^+).

Anal. Calcd for $\text{C}_{11}\text{H}_{23}\text{O}_3\text{PS}$: C, 49.61; H, 8.70; P, 11.63.

Found: C, 49.63; H, 8.99; P, 11.83.

O,O-Diethyl-(1-mercapto)-cyclopentane phosphonic acid ester (6b):

yield 26%; ir (neat) 2505(S-H), 1235(P=O), 1160 and 1030 cm^{-1} ; nmr (CCl_4) δ 1.34(t, 6H, $J=7.1\text{Hz}$, P-O- CH_2CH_3), 1.5-2.3(m, 8H, $-(\text{CH}_2)_4-$), 2.24(d, $J=4.5\text{Hz}$, 1H, SH) and 4.11 and 4.19(double q, 4H, $J_{\text{H-H}}=7.1\text{Hz}$, $J_{\text{P-H}}=8.5\text{Hz}$, P-O- CH_2CH_3); mass spectrum m/e 238(M^+).

Anal. Calcd for $\text{C}_9\text{H}_{19}\text{O}_3\text{PS}$: C, 45.36; H, 8.04; P, 13.00.

Found: C, 45.36; H, 7.96; P, 13.04.

O,O-Di-iso-propyl-(1-mercapto)-cyclopentane phosphonic acid ester (6c):

bp 107-109°C(3.2 mmHg); yield 83%; ir (neat) 2510(S-H), 1245 (P=O) and 980 cm^{-1} ; nmr (CDCl_3) δ 1.35(d, 12H, $J=6.5\text{Hz}$, P-O- $\text{CH}(\text{CH}_3)_2$), 1.55-2.20(m, 8H, $-(\text{CH}_2)_4-$), 2.28(d, 1H, $J=4.7\text{Hz}$, SH) and 4.78 and 4.86(double sep, 2H, $J_{\text{H-H}}=6.5\text{Hz}$, $J_{\text{P-H}}=8.0\text{Hz}$, P-O- $\text{CH}(\text{CH}_3)_2$); mass spectrum m/e 266(M^+).

Anal. Calcd for $\text{C}_{11}\text{H}_{23}\text{O}_3\text{PS}$: C, 49.61; H, 8.70; P, 11.63.

Found: C, 49.30; H, 8.54; P, 11.91.

O,O-Dimethyl-(1-methylthio)-cyclohexane phosphonic acid ester (7a):

bp 102-104°C(1.5 mmHg); yield 70%. All spectral and analytical data were identical with those of the product of the reaction of cyclohexanethione with trimethyl phosphite.

O,O-Diethyl-(1-ethylthio)-cyclohexane phosphonic acid ester (7b):

bp 114-115°C(2.3 mmHg) as a mixture of 7b and 8b; yield 20%; ir (neat) 1240(P=O), 1165 and 1030 cm^{-1} ; nmr (CDCl_3) δ 1.24(t, 3H, $J=7.5\text{Hz}$, S- CH_2CH_3), 1.35(t, 6H, $J=7.0\text{Hz}$, P-O- CH_2CH_3), 1.45-1.98(m, 10H, $-(\text{CH}_2)_5-$), 2.78(q, 2H, $J=7.5\text{Hz}$, S- CH_2CH_3) and 4.15 and 4.23(double q, 4H, $J_{\text{H-H}}=7.0\text{Hz}$, $J_{\text{P-H}}=8.0\text{Hz}$, P-O- CH_2CH_3); mass spectrum m/e 280(M^+).

Anal. Calcd for $C_{12}H_{25}O_3PS$: C, 51.41; H, 8.99; P, 11.05.

Found: C, 51.01; H, 8.82; P, 11.39.

O,O-Diethyl-(1-mercapto)-cyclohexane phosphonic acid ester (8b):

yield 30%; ir (neat) 2500(S-H), 1245(P=O), 1165 and 1025 cm^{-1} ; nmr ($CDCl_3$) δ 1.37(t, 6H, $J=7.0Hz$, P-O- $\underline{CH_2CH_3}$), 1.5-1.93(m, 10H, $-(CH_2)_5-$), 1.93(d, 1H, $J=5.0Hz$, SH) and 4.18 and 4.26(double q, 4H, $J_{H-H}=7.0Hz$, $J_{P-H}=8.0Hz$, P-O- $\underline{CH_2CH_3}$); mass spectrum m/e 252(M^+).

Anal. Calcd for $C_{10}H_{21}O_3PS$: C, 47.60; H, 8.39; P, 12.28.

Found: C, 47.71; H, 8.64; P, 12.47.

O,O-Di-iso-propyl-(1-mercapto)-cyclohexane phosphonic acid ester (8c):

bp 114-115°C(2.5 mmHg); yield 89%; ir (neat) 2500(S-H), 1245(P=O) and 990 cm^{-1} ; nmr ($CDCl_3$) 1.33(d, 12H, $J=7.0Hz$, P-O- $\underline{CH(CH_3)_2}$), 1.46-1.90(m, 10H, $-(CH_2)_5-$), 1.91(d, 1H, $J=4.5Hz$, SH) and 4.67 and 4.73(double sep, 2H, $J_{H-H}=7.0Hz$, $J_{P-H}=7.5Hz$, P-O- $\underline{CH(CH_3)_2}$); mass spectrum m/e 280(M^+).

Anal. Calcd for $C_{12}H_{25}O_3PS$: C, 51.41; H, 8.98; P, 11.05.

Found: C, 51.56; H, 9.23; P, 11.16.

O,O-Dicrotyl-(1-methylallylthio)-cyclohexane phosphonic acid ester

(11a): bp 149-150°C(4.0 mmHg); yield 65%; ir (neat) 3080, 3015, 1675, 1630, 1245(P=O) and 910(terminal vinyl) cm^{-1} ; nmr (CCl_4) 1.37(d, 3H, $J=7.5Hz$, S- $\underline{CH(CH_3)-CH=CH_2}$), 1.41-2.25(m, 16H, $-(CH_2)_5-$, and O- $\underline{CH_2-CH=CH-CH_3}$), 4.05-4.81(m, 5H, O- $\underline{CH_2-CH=CHCH_3}$ and S- $\underline{CH(CH_3)-CH=CH_2}$), 4.83-5.21(m, 2H, S- $\underline{CH(CH_3)-CH=CH_2}$) and 5.51-5.85(m, 5H, O- $\underline{CH_2CH=CHCH_3}$ and S- $\underline{CH(CH_3)-CH=CH_2}$); mass spectrum m/e 385(M^+).

Anal. Calcd for $C_{18}H_{31}O_3PS$: C, 60.30; H, 8.71; P, 8.64.

Found: C, 60.19; H, 8.85; P, 8.71.

O,O-Dimethylallyl-(1-crotylthio)-cyclohexane phosphonic acid ester

(11b): bp 110-111°C(0.5 mmHg); yield 58%; ir (neat) 3080, 3013, 1670, 1630, 1240(P=O) and 910 cm^{-1} ; nmr (CCl_4) 1.38(d, 6H, $J=7.4\text{Hz}$, $\text{O-CH}(\text{CH}_3)\text{-CH=CH}_2$), 1.45-2.08(m, 13H, $\text{-(CH}_2)_5\text{-}$ and $\text{S-CH}_2\text{-CH=CHCH}_3$), 3.36(d, 2H, $J=7.0\text{Hz}$, $\text{S-CH}_2\text{-CH=CHCH}_3$), 4.15-4.67(m, 2H, $\text{O-CH}(\text{CH}_3)\text{-CH=CH}_2$) and 4.57-6.23(m, 8H, $\text{O-CH}(\text{CH}_3)\text{-CH=CH}_2$ and $\text{S-CH}_2\text{-CH=CHCH}_3$); mass spectrum m/e 385(M^+).

Anal. Calcd for $\text{C}_{18}\text{H}_{31}\text{O}_3\text{PS}$: C, 60.30; H, 8.71; P, 8.64.

Found: C, 60.47; H, 8.93; P, 8.50.

O,O-Dimethyl-(1-methylthio)-cycloheptane phosphonic acid ester (9a):

bp 126-128°C(2.0 mmHg); yield 48%; ir (neat) 1240 (P=O), 1180 and 1040 cm^{-1} ; nmr (CDCl_3) δ 1.45-1.85(m, 12H, $\text{-(CH}_2)_6\text{-}$), 2.21(s, 3H, SCH_3) and 3.81(d, 6H, $J=10.0\text{Hz}$, P-O-CH_3); mass spectrum m/e 252(M^+).

Anal. Calcd for $\text{C}_{10}\text{H}_{21}\text{O}_3\text{PS}$: C, 47.60; H, 8.39; P, 12.28.

Found: C, 47.83; H, 8.54; P, 11.98.

O,O-Diethyl-(1-ethylthio)-cycloheptane phosphonic acid ester (9b):

bp 132-134°C(2.5 mmHg) as a mixture of 9b and 10b; yield 23%; ir (neat) 1235(P=O), 1160 and 1040 cm^{-1} ; nmr (CDCl_3) 1.24(t, 3H, $J=7.5\text{Hz}$, $\text{S-CH}_2\text{CH}_3$), 1.32(t, 6H, $J=7.0\text{Hz}$, $\text{P-O-CH}_2\text{CH}_3$), 1.45-1.93(m, 12H, $\text{-(CH}_2)_6\text{-}$), 2.78(q, 2H, $J=7.5\text{Hz}$, $\text{S-CH}_2\text{CH}_3$) and 4.11 and 4.19(double q, 4H, $J_{\text{H-H}}=7.0\text{Hz}$, $J_{\text{P-H}}=8.0\text{Hz}$, $\text{P-O-CH}_2\text{CH}_3$); mass spectrum m/e 294(M^+).

Anal. Calcd for $\text{C}_{13}\text{H}_{27}\text{O}_3\text{PS}$: C, 53.04; H, 9.24; P, 10.52.

Found: C, 52.75; H, 9.48; P, 10.73.

O,O-Diethyl-(1-mercapto)-cycloheptane phosphonic acid ester (10b):

yield 21%; ir (neat) 2505(S-H), 1245(P=O), 1160 and 1038 cm^{-1} ; nmr (CDCl_3) δ 1.38(t, 6H, $J=7.0\text{Hz}$, $\text{P-O-CH}_2\text{CH}_3$), 1.50-1.95(m, 12H, $\text{-(CH}_2)_6\text{-}$),

2.25(d,1H,J=5.0Hz,SH) and 4.19 and 4.27(double q,4H, $J_{H-H}=7.0\text{Hz}$, $J_{P-H}=8.0\text{Hz}$,P-O-CH₂CH₃); mass spectrum m/e 266(M⁺).

Anal. Calcd for C₁₁H₂₃O₃PS: C,49.61; H,8.70; P,11.63.

Found: C,49.89; H,8.96; P,11.52.

O,O-Di-iso-propyl-(1-mercapto)-cycloheptane phosphonic acid ester (10c): bp 141-142°C(2.9 mmHg); yield 76%; ir (neat) 2500(S-H), 1240(P=O) and 990 cm⁻¹; nmr (CCl₄) δ 1.32(d,12H,J=6.5Hz,P-O-CH(CH₃)₂), 1.42-2.20(m,12H,-(CH₂)₆-), 2.11(d,1H,J=4.6Hz,SH) and 4.69 and 4.76(double sep,2H, $J_{H-H}=6.5\text{Hz}$, $J_{P-H}=7.5\text{Hz}$,P-O-CH(CH₃)₂); mass spectrum m/e 294(M⁺).

Anal. Calcd for C₁₃H₂₇O₃PS: C,53.04; H,9.24; P,10.52.

Found: C,53.32; H,9.42; P,10.61.

Reaction of Cyclohexanedithiol with Trimethyl Phosphite in Ethanol.

A mixture of 3 (1.48g) and trimethyl phosphite (5.0g) in 20 ml of ethanol was heated at reflux temperature under nitrogen for 5 hr. After concentration, the residue was distilled to afford 1.4g of a mixture of 7a and 8a, which were separated by gas chromatography and yields were determined. The yields of 7a was 23 %, all spectral data were identical with 7a.

O,O-Dimethyl-(1-mercapto)-cyclohexane phosphonic acid ester (8a): mp 31-32°C; yield 39%; ir (neat) 2510(S-H), 1230(P=O), 1180 and 1040 cm⁻¹; nmr (CDCl₃) δ 1.43-1.98(m,10H,-(CH₂)₅-), 1.93(d,1H,J=4.5Hz,SH) and 3.85(d,6H,J=10.0Hz,P-O-CH₃); mass spectrum m/e 224(M⁺).

Anal. Calcd for C₈H₁₇O₃PS: C,42.85; H,7.64; P,13.81.

Found: C,42.83; H,7.66; P,13.68.

Reaction of 2,2,4,4-Tetramethyl-Cyclobutane-1,3-dithione with trimethyl Phosphite. A mixture of 2,2,4,4-tetramethyl cyclobutane-1,3-dithione (1.37g) and 4 equivalent trimethyl phosphite in 20 ml of toluene was heated at reflux temperature under nitrogen for 3 hr. After concentration, the residue was chromatographed on silica with the elution of benzene to give 1.35 g of orange liquid, whose spectral data were all identical with the authentic sample 15.²⁹

Reaction of Diphenylcyclopropenethione with Trimethyl Phosphite.

To a solution of diphenylcyclopropenethione (111mg) in 20 ml toluene was added dropwise equivalent trimethyl phosphite at 0° with stirring under nitrogen. After 30 min, 2 ml of methanol was added to the solution and the reaction mixture was allowed to stand at room temperature for an hour. After removal of toluene and trimethyl phosphite, the residue was subjected to silicagel column chromatograph eluting with benzene and orange crystals, methyl α -phenyl-trans-thiocinnamate (17), was obtained: mp 63.0-63.5°C; yield 89%; ir (KBr) 3050, 3035, 2945, 1615, 1450, 1240(C=S) and 1146(OCH₃) cm⁻¹; nmr (CDCl₃) δ 4.13(s, 3H, OCH₃), 6.87-7.42(m, 10H, C₆H₅) and 7.99(s, 1H, C=CH); mass spectrum m/e 254(M⁺).

Anal. Calcd for C₁₆H₁₃OS: C, 75.55; H, 5.55; O, 6.29; S, 12.61.
Found: C, 75.64; H, 5.55; O, 6.42; S, 12.87.

Reduction by Raney Ni. To a suspended solution of 10-15 g of Raney Ni (W-2 type) in 50 ml of ethanol was added a solution containing phosphonic acid esters (5-10) [1.5-2.0 g in 5 ml of ethanol]. The reaction mixture was heated at reflux temperature for 20 hr. After

filtration of nickel, the filtrate was concentrated and the residue was distilled to afford cycloalkane phosphonic acid esters (18-20). The yields were summarized in Table 2.

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CHAPTER II

REACTION OF ALIPHATIC THIONES WITH TRIALKYL PHOSPHITES

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Submitted to J. Org. Chem.,

SUMMARY

Several aliphatic thiones were reacted with trimethyl, triethyl and tri-iso-propyl phosphites at 110° to give alkylthio- and/or mercapto-alkane phosphonic acid esters. This reaction is interpreted in terms of carbophilic attack by phosphites at the carbon atom of thiocarbonyl group, and followed by the concerted migration mechanism via the betaine intermediate.

INTRODUCTION

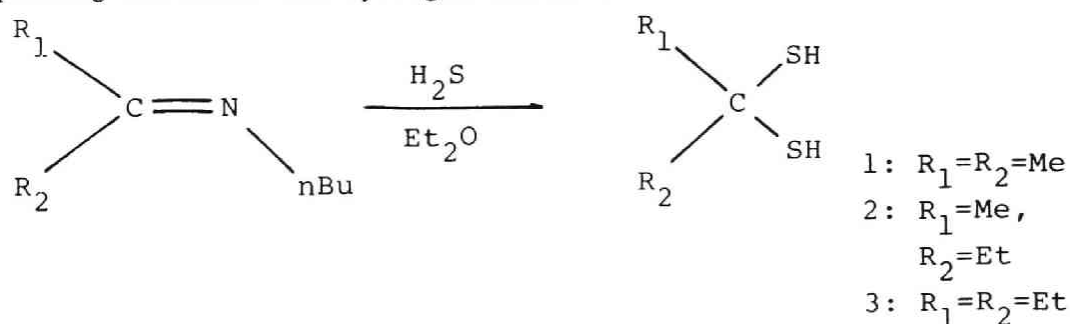
It is known that the reactions of thiocarbonyl compounds with nucleophiles are different from those of carbonyl compounds. For example, though Grignard reagents normally attack at the carbon atom of carbonyl group (carbophilic attack), Grignard reagents would attack at the sulfur atom of thiocarbonyl group (thiophilic attack) rather than at the carbon atom.¹

When trivalent phosphorus compounds (phosphines and phosphites) are employed as nucleophiles, they have generally been regarded as thiophile, not as carbophile, in the previous reported works.² However, thiocarbonyl compounds used in those works were aromatic,^{2b,f} perfluoro thiones^{2b} and cyclic trithiocarbonates.^{2a,c-e,g} In chapter I it is elucidated that cycloalkanethiones react with trialkyl phosphites, which attack at the carbon atom of thiocarbonyl group to give phosphonic acid esters.

In this chapter, it is described that in the reactions of aliphatic thiocarbonyl compounds (thioacetone, methyl ethyl thioketone and diethyl thioketone) with trialkyl phosphites, phosphites also attack at the thiocarbonyl carbon atom and give the sulfur containing phosphonic acid esters.

RESULTS AND DISCUSSION

In the preceeding chapter I, cycloalkanedithiols were utilized as precursors of cycloalkanethiones for the latter unstability. Cycloalkanedithiols facilely generate the corresponding cycloalkanethiones at elevated temperature. Similarly, as precursors of thioacetone, methyl ethyl thioketone and diethyl thioketone, gem-dithiols are employed in this chapter, which were easily prepared from the corresponding ketimines and hydrogen sulfide.³

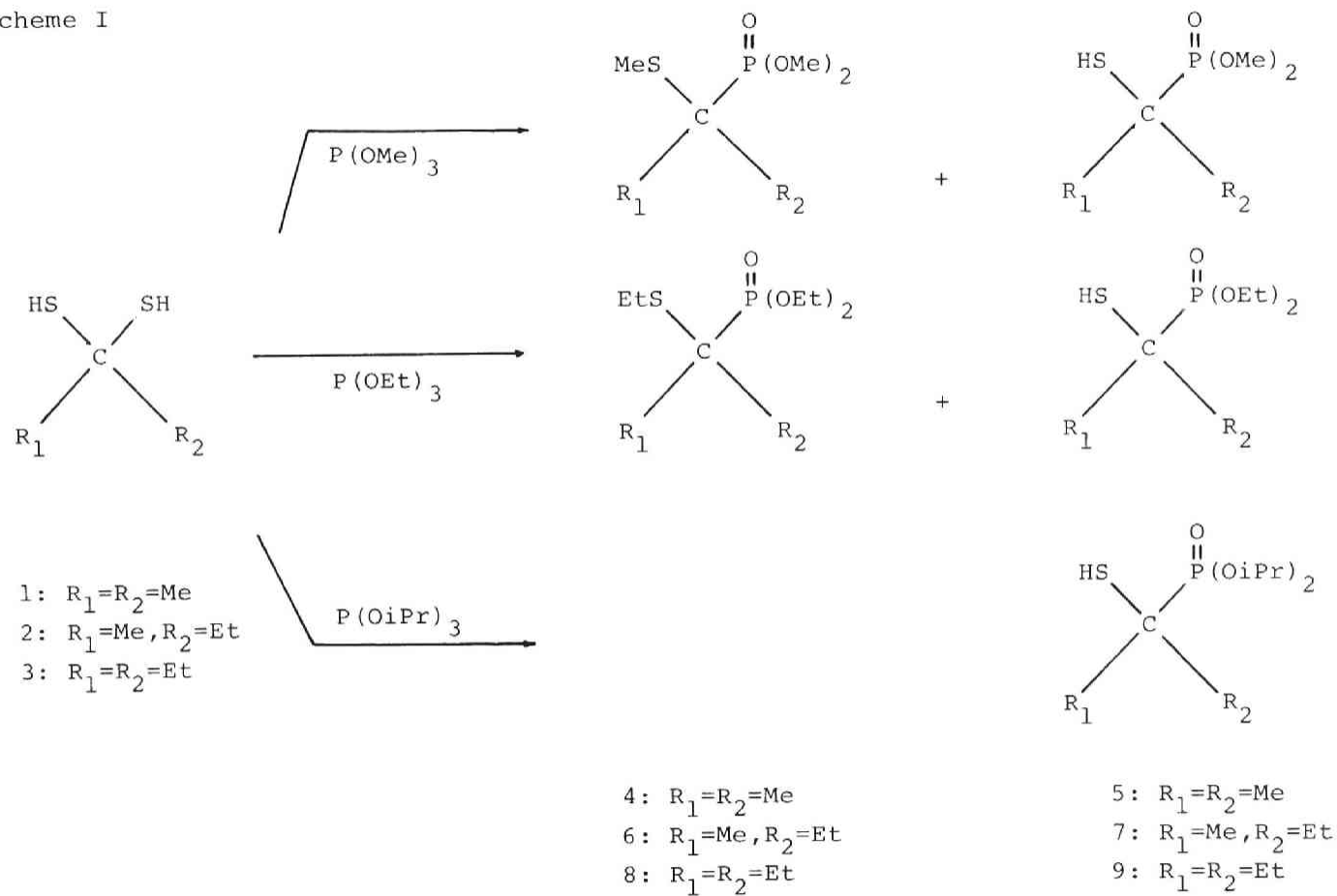


Reaction of thioacetone with trialkyl phosphites. When a solution of propane-2-dithiol (1) and four equivalents of trimethyl phosphite in toluene was heated to reflux temperature under nitrogen, hydrogen sulfide evolved vigorously and the color of the reaction mixture turned to pink. The evolution of hydrogen sulfide and pink coloration

indicate the formation of thioacetone in the reaction. After the complete decolorization, distillation of the reaction mixture gave a mixture of O,O-dimethyl-(2-methylthio)-propane-2-phosphonic acid ester (4a) and O,O-dimethyl-(2-mercapto)-propane-2-phosphonic acid ester (5a), which were separated and analysed by gas chromatography. The structures were determined by the elemental analyses and spectral data. In the nmr spectrum of 4a, the protons of the methyl group attached to the sulfur atom appeared as a singlet at δ 2.28 and those attached to the oxygen atom as a doublet at δ 3.80 with $J_{P-H}=10.0\text{Hz}$. The infrared spectrum of 4a revealed a strong band at 1255 cm^{-1} attributable to a P=O double bond. On the other hand, in the nmr spectrum of 5a, the resonances of the methyl group attached to the sulfur atom disappeared, and the mercapto proton appeared as a doublet at δ 2.16 with $J_{P-H}=4\text{Hz}$. The infrared spectrum of 5a exhibited an absorption at 2500 cm^{-1} assigned to SH stretching, but the absorption was not so strong probably because of the hydrogen bonding between SH and P=O groups. In this reaction, the distillation residue contained hexamethyltrithiane in 30-40% yield.

The reaction of 1 with triethyl phosphite also gave a mixture of O,O-diethyl-(2-ethylthio)-propane-2-phosphonic acid ester (4b) and O,O-diethyl-(2-mercapto)-propane-2-phosphonic acid ester (5b). The structures were determined by the spectral data after separated by gas chromatography. The nmr spectrum of 4b consisted of a quartet at δ 2.78(2H, $J=7.5\text{Hz}$, SCH_2CH_3), double quartets at 4.03(4H, $J_{H-H}=7.0\text{Hz}$, $J_{P-H}=8.0\text{Hz}$, POCH_2CH_3) and two triplets at δ 1.13(3H, $J=7.5\text{Hz}$, SCH_2CH_3) and

Scheme I



1.25(6H, $J=7.0\text{Hz}$, POCH_2CH_3). In the nmr spectrum of 5b, the resonances of ethyl group attached to the sulfur atom disappeared, and the mercapto proton appeared as a doublet at δ 2.16 with $J_{\text{P-H}}=4\text{Hz}$, the methylene protons as double quartets at δ 4.05, and the methyl protons as a triplet at δ 1.26 with $J_{\text{H-H}}=7.0\text{Hz}$ and $J_{\text{P-H}}=8.5\text{Hz}$, respectively. The infrared spectrum of 5b revealed a weak absorption of SH stretching at 2503 cm^{-1} together with a P=O stretching at 1245 cm^{-1} .

The reaction of 1 with tri-iso-propyl phosphite gave only 0,0-di-iso-propyl-(2-mercapto)-propane-2-phosphonic acid ester (5c), but no ester having an alkylthio group was obtained. Similar to 5a and 5b, in the nmr spectrum the mercapto proton appeared at 2.24 and in the infrared spectrum a weak band appeared at 2500 cm^{-1} .

Reaction of methyl ethyl thioketone. The reaction of 2 with trimethyl phosphite was carried out at reflux temperature under nitrogen and after the complete decolorization distillation also gave a mixture of 0,0-dimethyl-(2-methylthio)-butane-2-phosphonic acid ester (6a) and 0,0-dimethyl-(2-mercapto)-butane-2-phosphonic acid ester (7a). The structures were determined by the spectral data. In the nmr spectrum of 6a, the methyl protons attached to the sulfur atom appeared as a singlet at δ 2.19, but, different from those of 4a, the protons of methyl group attached to the oxygen atom appeared as two doublets at δ 3.73 and 3.79. The appearance of two kinds of doublets (1:1) with $J_{\text{P-H}}=10.0\text{Hz}$ is reasonably explained by the following considerations that the attack of trimethyl phosphite at the thiocarbonyl group of methyl ethyl thioketone from the different side of the mole-

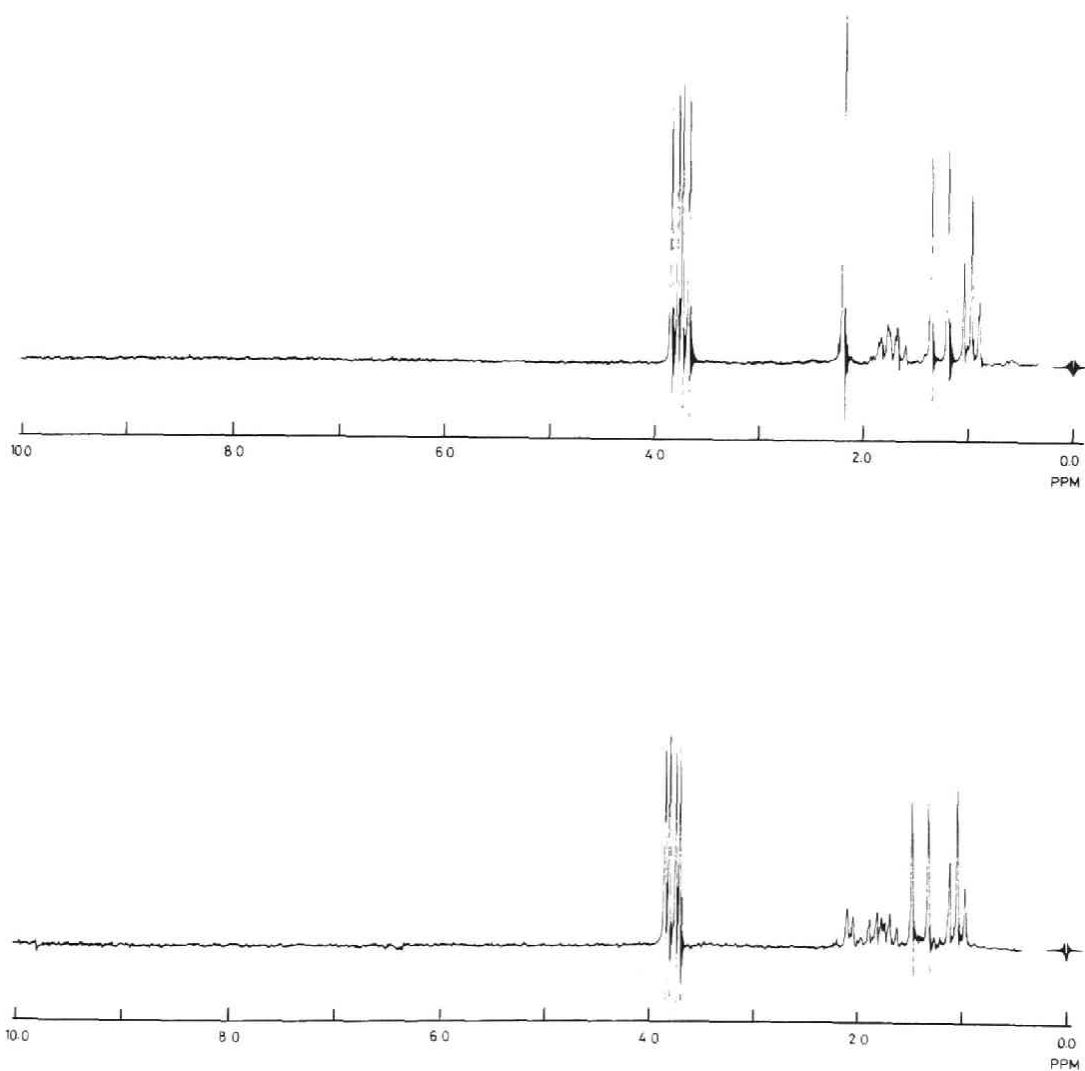
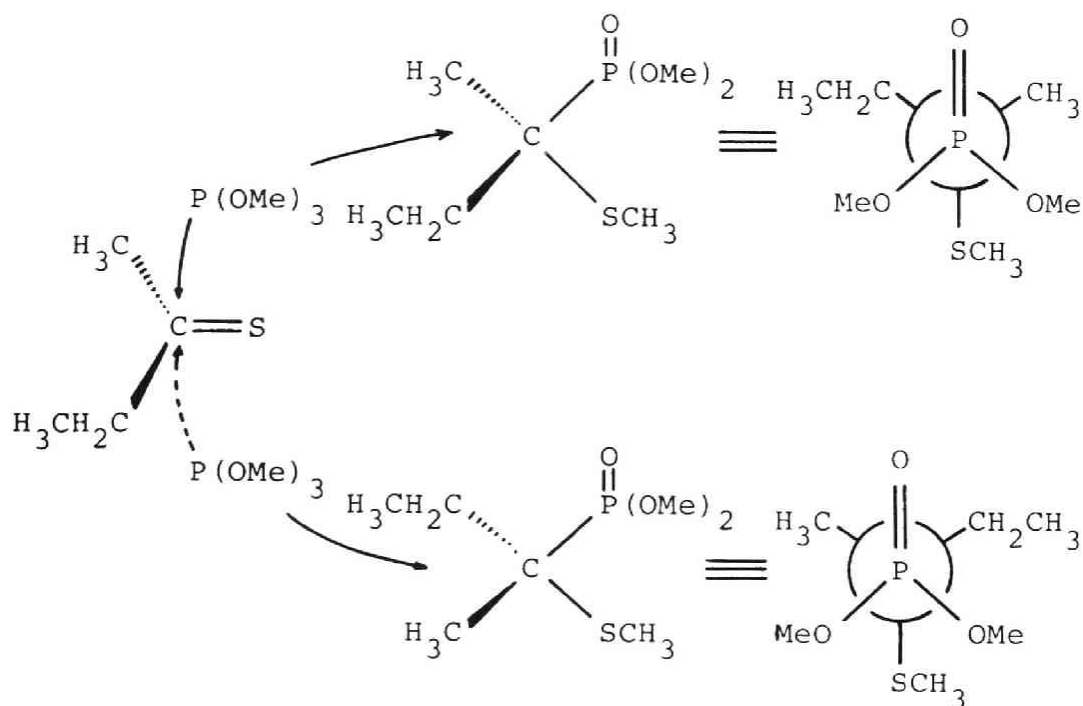


Fig. 1. ^1H -NMR Spectra of O,O-Dimethyl-(2-methylthio)- (6a) and O,O-Dimethyl-(2-mercapto)-butane-2-phosphonic Acid Ester (7a).

cular plane would determine the absolute configurations (R- and S-), whose ratio must be 1:1 and , as a result, the differences of environment of R- and S-configurations cause the difference in chemical shifts. The protons of the methyl and methylthio groups appeared as singlets owing to the free rotation. On the other hand, the ethyl group would be hindered to rotate, and so the methylene protons would appear as multiplet because of coupling with the methyl protons and coupling with phosphorus atom as well as the presence of R- and S-configurations. These observations appeared in the products by the reaction of methyl ethyl thioketone with triethyl and tri-iso-propyl phosphites. The nmr spectra of 6a and 7a are illustrated in Fig. 1.



In the nmr spectrum of 7a, the resonances of methyl group attached to the sulfur atom disappeared, and the mercapto proton appear-

ed as a doublet at δ 2.07 together with two kinds of doublets at δ 3.76 and 3.80. The infrared spectrum of 7a revealed a weak band at 2520 cm^{-1} assigned to the SH stretching.

The reaction of 2 with triethyl phosphite also gave a mixture of O,O-diethyl-(2-ethylthio)-butane-2-phosphonic acid ester (6b) and O,O-diethyl-(2-mercapto)-butane-2-phosphonic acid ester (7b). The nmr spectrum of 6b consisted of two kinds of ethyl groups, and the methylene protons of the ethylthio group appeared as two kinds of quartets because of the absolute configurations mentioned above. In the nmr spectrum of 7b, the mercapto proton appeared at δ 2.04 together with two kinds of double quartets of POCH_2CH_3 . The infrared spectrum of 7b clearly exhibited an absorption at 2510 cm^{-1} assigned to the SH group.

A similar reaction of 2 with tri-iso-propyl phosphite gave only one product, O,O-di-iso-propyl-(2-mercapto)-butane-2-phosphonic acid ester (7c). This product showed the SH absorption band at 2505 cm^{-1} in the infrared spectrum and the signal at δ 2.07 in the nmr spectrum together with two kinds of double septets of $\text{POCH}(\text{CH}_3)_2$.

Reaction of diethyl thioketone. The reaction of 3 with trimethyl phosphite was carried out in a similar manner and the evolution of hydrogen sulfide and the pink coloration were observed. After the complete decolorization, the distillation afforded a mixture of O,O-dimethyl-(3-methylthio)-pentane-3-phosphonic acid ester (8a) and O,O-dimethyl-(3-mercapto)-pentane-3-phosphonic acid ester (9a) in the ratio 4:1. In the nmr spectra of 8a and 9a, the methyl protons at-

Table 1. Reaction Conditions and Yields of Products in the Reaction of
Aliphatic Alkanedithiols with Trialkyl Phosphites

Substrates (gem-dithiols)	Reactants (phosphites)	Reaction Time (hr)	Solvents	Yield (%)	
				alkylthio	mercapto
propane-2- dithiol (1)*	P(OMe) ₃	20	toluene	23	23
	P(OEt) ₃	20	toluene	25	17
	P(OiPr) ₃	20	toluene	0	62
butane-2- dithiol (2)	P(OMe) ₃	20	toluene	35	18
	P(OEt) ₃	25	toluene	17	24
	P(OiPr) ₃	20	toluene	0	76
pentane-2- dithiol (3)	P(OMe) ₃	30	toluene	43	11
	P(OEt) ₃	30	toluene	24	29
	P(OiPr) ₃	20	toluene	0	80

*: In the reaction of 1, hexamethyl trithiane was obtained in 30-40% yield.

tached to the oxygen atom appeared as a doublet at δ 3.76 and 3.77, respectively.

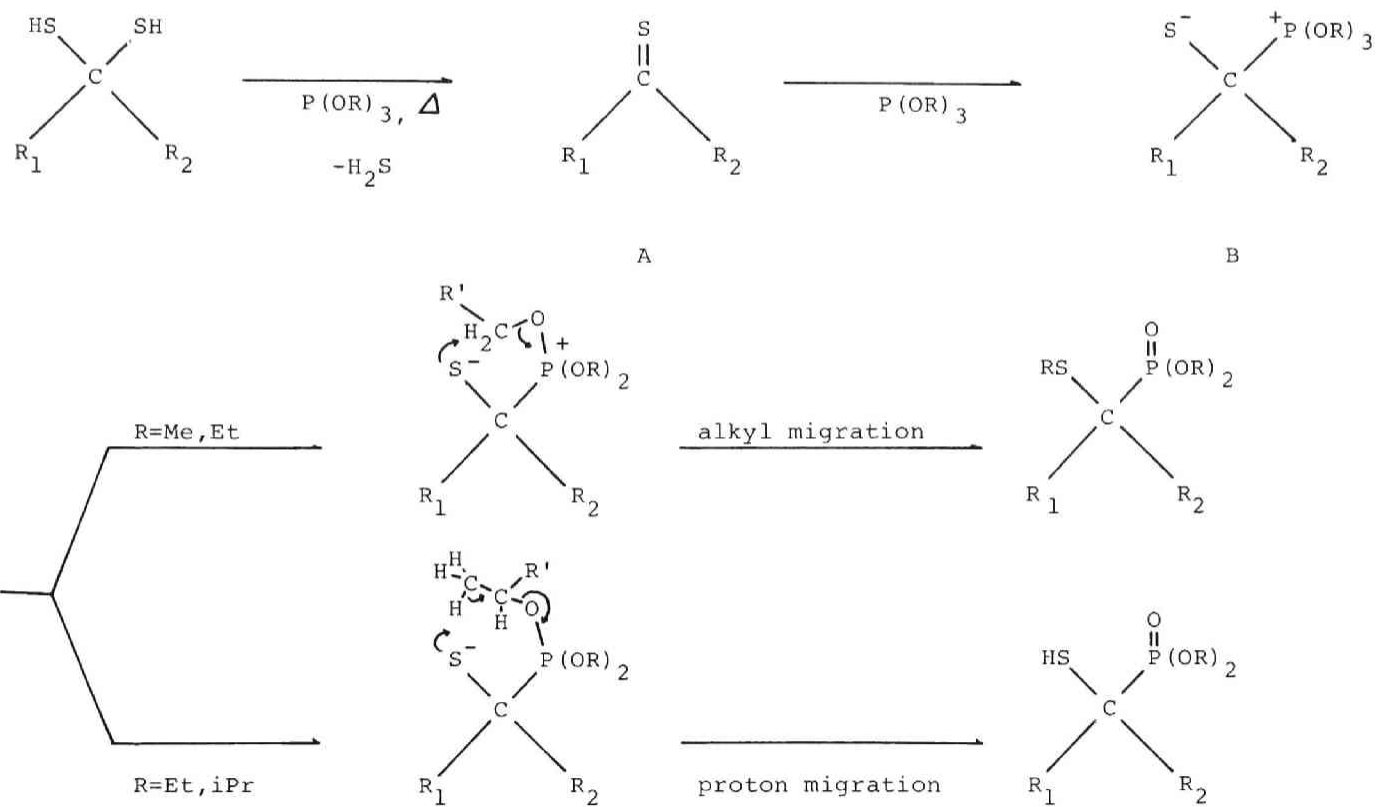
The reaction of 3 with triethyl phosphite gave a mixture of 0, 0-diethyl-(3-ethylthio)-pentane-3-phosphonic acid ester (8b) and 0,0-diethyl-(3-mercapto)-pentane-3-phosphonic acid ester (9b). Their structures were determined by the spectral data in a similar manner mentioned above. The nmr spectrum of 8b consisted of two kinds of ethyl groups (SCH_2CH_3 and POCH_2CH_3) and in the nmr spectrum of 9b the mercapto proton appeared at δ 2.10.

The reaction of 3 with tri-iso-propyl phosphite gave only 0,0-di-iso-propyl-(3-mercapto)-pentane-3-phosphonic acid ester (9c). The structure of 9c was supported by the SH absorption band at 2500 cm^{-1} in the infrared spectrum and the signal assigned to SH at δ 2.05 in the nmr spectrum.

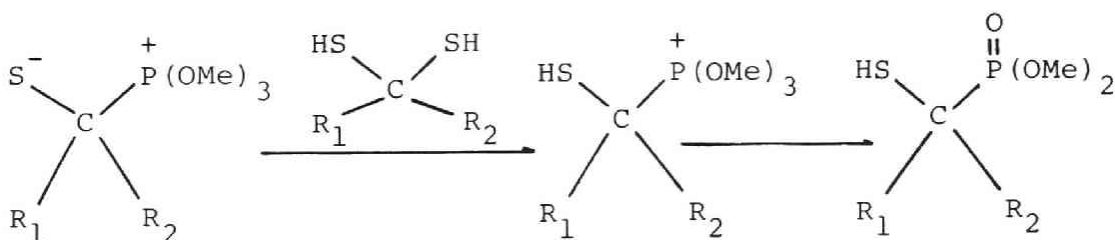
These results are summarized in Scheme 1 and in Table 1.

The mechanistic interpretation of the reactions of aliphatic thioketones with trialkyl phosphites is outlined in Scheme 2. As is the case with the reactions of cycloalkanethiones with trialkyl phosphites, the reaction is initiated by the removal of hydrogen sulfide from gem-dithiols to form the corresponding thioketones (A). The resulting thioketones might immediately react with excess trialkyl phosphites. The phosphites should attack at the carbon atom of the thio-carbonyl group and form the betaine intermediate (B), just as the case of cycloalkanethiones. Then, as the phosphites attack at the carbon atom equally from the different side of molecular plane, R- and S-

Scheme II



configured intermediates would be formed by 1:1 when methyl ethyl thioketone was employed. From the intermediate B the migration of alkyl group or proton would afford the phosphonic acid esters containing sulfur atom as alkylthio or mercapto groups. When phosphites were trimethyl and/or triethyl phosphites, the negatively charged sulfur atom would intramolecularly attack the alkyl groups attached to the oxygen atom from backside and result in the formation of alkylthio phosphonic acid esters. However, when triethyl and/or triisopropyl phosphites were used, these backside attack should be hindered, and so the proton migration would occur to afford the mercapto phosphonic acid esters. However, even when the trimethyl phosphite was used, the mercapto phosphonic acid esters were obtained in fair yields, whose formation can be explained by the following scheme.



The betaine intermediate B would abstract the acidic proton of gem-dithiols, since the dehydrogen sulfide reaction of gem-dithiols to thioketones are not so fast as the case of cycloalkanedithiols because of the low boiling points of dithiols (1-3). However, as the boiling points coming higher, the product ratio of mercapto esters to methylthio esters decreased.

EXPERIMENTAL

The infrared spectra were recorded on a Hitachi EPI-3G grating infrared spectrophotometer, the nmr spectra were recorded on a Varian Associate AH-100 spectrometer and mass spectra were taken on Hitachi RMU-6C. Gas-liquid chromatography was carried out with a Shimadzu gas chromatograph Model GC-6A and separation was carried out on a Varian Aerograph Model 920 using 20% silicon DC550. Elemental analyses were carried out at the Elemental Analytical Center of Kyoto University.

Materials. Propane-2-dithiol (1), butane-2-dithiol (2) and pentane-3-dithiol (3) were prepared from the corresponding ketimines by the reaction with hydrogen sulfide according to the literature of Magnusson³ and distilled under reduced pressure not to exceed 70°C. Trimethyl and triethyl phosphites were commercial materials and were used after distillation. Tri-iso-propyl phosphite was prepared utilizing the procedure of Ford-Moore and Jerry⁴ from phosphorus trichloride and iso-propyl alcohol.

General Procedure for Reactions of Alkanedithiols (1-3) with Trialkyl Phosphites. A mixture of 0.01 mole of alkanedithiol (1-3) and 0.04 mole of trialkyl phosphite in 30 ml of toluene was heated at reflux temperature under nitrogen for 20-30 hr. When the temperature of the reaction mixture exceeded 80°C, the gas evolution and pink coloration were observed. After removal of toluene and excess trialkyl phosphite, the residue was distilled under reduced pressure to give colorless viscous liquid. In the reaction with trimethyl and

triethyl phosphites, the distillates were mixtures of alkylthio- and mercapto-alkane phosphonic acid esters, which were separated by gas chromatography and yields were determined.

The boiling points and ir, nmr and mass spectral data and the results of elemental analyses are as following:

O,O-Dimethyl-(2-methylthio)-propane-2-phosphonic acid ester (4a):

bp 78-80°C(14 mmHg) as a mixture of 4a and 5a; yield 22.8%; ir (neat) 1255(P=O), 1180, 1060, 1030, 830 and 800 cm^{-1} ; nmr (CCl_4) δ 1.49(d, 6H, $J_{\text{P-H}}=15.5\text{Hz}$, CH_3), 2.28(s, 3H, SCH_3) and 3.80(d, 6H, $J_{\text{P-H}}=10.0\text{Hz}$, POCH_3); mass m/e 198(M^+).

Anal. Calcd for $\text{C}_6\text{H}_{15}\text{O}_3\text{PS}$: C,36.36; H,7.63; P,15.63.

Found: C,36.53; H,7.86; P,15.66.

O,O-Dimethyl-(2-mercapto)-propane-2-phosphonic acid ester (5a): yield

22.7%; ir (neat) 2500(SH), 1250(P=O), 1180, 1060, 1025, 830 and 790 cm^{-1} ; nmr (CCl_4) δ 1.59(d, 6H, $J_{\text{P-H}}=15.5\text{Hz}$, CH_3), 2.16(d, 1H, $J_{\text{P-H}}=4\text{Hz}$, SH) and 3.78(d, 6H, $J_{\text{P-H}}=10.0\text{Hz}$, POCH_3); mass m/e 184(M^+).

Anal. Calcd for $\text{C}_5\text{H}_{13}\text{O}_3\text{PS}$: C,32.60; H,7.11; P,16.82.

Found: C,32.43; H,7.07; P,16.85.

O,O-Diethyl-(2-ethylthio)-propane-2-phosphonic acid ester (4b): bp

82-83°C(9 mmHg) as a mixture of 4b and 5b; yield 24.7%; ir (neat) 1250(P=O), 1060, 1030 and 963 cm^{-1} ; nmr (CCl_4) δ 1.13 (t, 3H, $J_{\text{H-H}}=7.5\text{Hz}$, SCH_2CH_3), 1.25(t, 6H, $J_{\text{H-H}}=7.0\text{Hz}$, POCH_2CH_3), 1.30(d, 6H, $J_{\text{P-H}}=15\text{Hz}$, CH_3), 2.78(q, 2H, $J_{\text{H-H}}=7.5\text{Hz}$, SCH_2CH_3) and 4.03(double q, 4H, $J_{\text{H-H}}=7.0\text{Hz}$, $J_{\text{P-H}}=8.0\text{Hz}$, POCH_2CH_3); mass m/e 240(M^+).

Anal. Calcd for $\text{C}_9\text{H}_{21}\text{O}_3\text{PS}$: C,44.98; H,8.81; P,12.89.

Found: C, 44.65; H, 9.08; P, 12.69.

O,O-Diethyl-(2-mercapto)-propane-2-phosphonic acid ester (5b): yield 17%; ir (neat) 2503(SH), 1245(P=O), 1050, 1023 and 955 cm^{-1} ; nmr (CCl_4) δ 1.26(t, 6H, $J_{\text{H-H}}=7.0\text{Hz}$, POCH_2CH_3), 1.40(d, 6H, $J_{\text{P-H}}=15.0\text{Hz}$, CH_3), 2.16(d, 1H, $J_{\text{P-H}}=4\text{Hz}$, SH) and 4.05(double q, 4H, $J_{\text{H-H}}=7.0\text{Hz}$, $J_{\text{P-H}}=8.5\text{Hz}$, POCH_2CH_3); mass m/e 212(M^+).

Anal. Calcd for $\text{C}_7\text{H}_{17}\text{O}_3\text{PS}$: C, 39.61; H, 8.07; P, 14.59.

Found: C, 39.67; H, 8.11; P, 14.41.

O,O-Di-iso-propyl-(2-mercapto)-propane-2-phosphonic acid ester (5c): bp 92-93°C(11 mmHg); yield 62%; ir (neat) 2500(SH), 1250(P=O), 1005 and 985 cm^{-1} ; nmr (CCl_4) δ 1.33(d, 12H, $J_{\text{H-H}}=6.5\text{Hz}$, $\text{POCH}(\text{CH}_3)_2$), 1.45(d, 6H, $J_{\text{P-H}}=15\text{Hz}$, CH_3), 2.24(d, 1H, $J_{\text{P-H}}=4\text{Hz}$, SH) and 4.64(double sep, 2H, $J_{\text{H-H}}=6.5\text{Hz}$, $J_{\text{P-H}}=8.5\text{Hz}$, $\text{POCH}(\text{CH}_3)_2$); mass m/e 240(M^+).

Anal. Calcd for $\text{C}_9\text{H}_{21}\text{O}_3\text{PS}$: C, 44.98; H, 8.81; P, 12.89.

Found: C, 44.65; H, 9.13; P, 12.51.

O,O-Dimethyl-(2-methylthio)-butane-2-phosphonic acid ester (6a): bp 98-99°C(13 mmHg) as a mixture of 6a and 7a; yield 34.5%; ir (neat) 1249(P=O), 1185, 1060, 1031, 823 and 780 cm^{-1} ; nmr (CCl_4) δ 0.97(t, 3H, $J_{\text{H-H}}=7.1\text{Hz}$, CH_2CH_3), 1.27(d, 3H, $J_{\text{P-H}}=15.5\text{Hz}$, CH_3), 1.58-1.97(m, 2H, CH_2CH_3), 2.19(s, 3H, SCH_3) and 3.73 and 3.79(two d, 6H, $J_{\text{P-H}}=10.0\text{Hz}$, POCH_3); mass m/e 212(M^+).

Anal. Calcd for $\text{C}_7\text{H}_{17}\text{O}_3\text{PS}$: C, 39.61; H, 8.07; P, 14.59.

Found: C, 39.58; H, 8.14; P, 14.49.

O,O-Dimethyl-(2-mercapto)-butane-2-phosphonic acid ester (7a): yield 18.2%; ir (neat) 2520(SH), 1252(P=O), 1186, 1060, 1034, 830 and 782

cm^{-1} ; nmr (CCl_4) δ 1.04(t, 3H, $J_{\text{H-H}}=7.5\text{Hz}$, CH_2CH_3), 1.40(d, 3H, $J_{\text{P-H}}=15.0\text{Hz}$, CH_3), 1.61-2.01(m, 2H, CH_2CH_3), 2.07(d, 1H, $J_{\text{P-H}}=5\text{Hz}$, SH), 3.76 and 3.80 (two d, 6H, $J_{\text{P-H}}=10.5\text{Hz}$, POCH_3); mass m/e 198(M^+).

Anal. Calcd for $\text{C}_6\text{H}_{15}\text{O}_3\text{PS}$: C, 36.36; H, 7.63; P, 15.63.

Found: C, 36.52; H, 7.42; P, 15.28.

O,O-Diethyl-(2-ethylthio)-butane-2-phosphonic acid ester (6b): bp 98-103°C(5.5 mmHg) as a mixture of 6b and 7b; yield 16.9%; ir (neat) 1245(P=O), 1058, 1030 and 960 cm^{-1} ; nmr (CCl_4) δ 0.98(t, 3H, $J_{\text{H-H}}=7.0\text{Hz}$, CH_2CH_3), 1.20(t, 3H, $J_{\text{H-H}}=7.5\text{Hz}$, SCH_2CH_3), 1.28(d, 3H, $J_{\text{P-H}}=15\text{Hz}$, CH_3), 1.32 and 1.33(two t, 6H, $J_{\text{H-H}}=7.0\text{Hz}$, POCH_2CH_3), 1.61-1.97(m, 2H, CH_2CH_3), 2.73 and 2.83(two q, 2H, $J_{\text{H-H}}=7.5\text{Hz}$, SCH_2CH_3), 4.08 and 4.13(two double q, 4H, $J_{\text{H-H}}=7.0\text{Hz}$, $J_{\text{P-H}}=8.0\text{Hz}$, POCH_2CH_3); mass m/e 254(M^+).

Anal. Calcd for $\text{C}_{10}\text{H}_{23}\text{O}_3\text{PS}$: C, 47.23; H, 9.12; P, 12.18.

Found: C, 47.10; H, 9.23; P, 12.25.

O,O-Diethyl-(2-mercapto)-butane-2-phosphonic acid ester (7b): yield 24.4%; ir (neat) 2510(SH), 1250(P=O), 1055, 1030 and 963 cm^{-1} ; nmr (CCl_4) δ 1.06(t, 3H, $J_{\text{H-H}}=7.0\text{Hz}$, CH_2CH_3), 1.34(t, 6H, $J_{\text{H-H}}=7.0\text{Hz}$, POCH_2CH_3), 1.40(d, 3H, $J_{\text{P-H}}=15.5\text{Hz}$, CH_3), 1.60-1.93(m, 2H, CH_2CH_3), 2.04(d, 1H, $J_{\text{P-H}}=6\text{Hz}$, SH), 4.12 and 4.15(two double q, 4H, $J_{\text{H-H}}=7.0\text{Hz}$, $J_{\text{P-H}}=8.0\text{Hz}$, POCH_2CH_3); mass m/e 226(M^+).

Anal. Calcd for $\text{C}_8\text{H}_{19}\text{O}_3\text{PS}$: C, 42.46; H, 8.46; P, 13.69.

Found: C, 42.62; H, 8.64; P, 13.47.

O,O-Di-iso-propyl-(2-mercapto)-butane-2-phosphonic acid ester (7c): bp 100-101°C(6.7 mmHg); yield 76%; ir (neat) 2505(SH), 1246(P=O), 1108, 1005 and 980 cm^{-1} ; nmr (CCl_4) δ 1.04(t, 3H, $J_{\text{H-H}}=7.0\text{Hz}$, CH_2CH_3), 1.32(

d, 12H, $J_{\text{H-H}}=6\text{Hz}$, $\text{POCH}(\underline{\text{CH}_3})_2$), 1.40(d, 3H, $J_{\text{P-H}}=13.0\text{Hz}$, CH_3), 1.54-1.97(m, 2H, $\underline{\text{CH}_2\text{CH}_3}$), 2.07(d, 1H, $J_{\text{P-H}}=6\text{Hz}$, SH), 4.35-4.96(m, 2H, $\text{POCH}(\underline{\text{CH}_3})_2$); mass m/e 254(M^+).

Anal. Calcd for $\text{C}_{10}\text{H}_{23}\text{O}_3\text{PS}$: C, 47.23; H, 9.12; P, 12.18.

Found: C, 47.31; H, 9.36; P, 11.92.

O,O-Dimethyl-(3-methylthio)-pentane-3-phosphonic acid ester (8a): bp 111-112°C(6.5 mmHg) as a mixture of 8a and 9a; yield 42.9%; ir (neat) 1246(P=O), 1182, 1060, 1031, 824 and 770 cm^{-1} ; nmr (CCl_4) δ 0.95(t, 6H, $J_{\text{H-H}}=7.1\text{Hz}$, $\underline{\text{CH}_2\text{CH}_3}$), 1.54-1.97(m, 4H, $\underline{\text{CH}_2\text{CH}_3}$), 2.18(s, 3H, SCH_3) and 3.76(d, 6H, $J_{\text{P-H}}=10.2\text{Hz}$, POCH_3); mass m/e 226(M^+).

Anal. Calcd for $\text{C}_8\text{H}_{19}\text{O}_3\text{PS}$: C, 42.46; H, 8.46; P, 13.69.

Found: C, 42.37; H, 8.62; P, 13.90.

O,O-Dimethyl-(3-mercapto)-pentane-3-phosphonic acid ester (9a): yield 10.9%; ir (neat) 2500(SH), 1245(P=O), 1060, 1030, 820 and 770 cm^{-1} ; nmr (CCl_4) δ 1.00(t, 6H, $J_{\text{H-H}}=6.5\text{Hz}$, $\underline{\text{CH}_2\text{CH}_3}$), 1.73 and 1.87(double q, 4H, $J_{\text{H-H}}=6.5\text{Hz}$, $J_{\text{P-H}}=13.5\text{Hz}$, $\underline{\text{CH}_2\text{CH}_3}$), 2.03(d, 1H, $J_{\text{P-H}}=6\text{Hz}$, SH) and 3.77(d, 6H, $J_{\text{P-H}}=10.1\text{Hz}$, POCH_3); mass m/e 212(M^+).

Anal. Calcd for $\text{C}_7\text{H}_{17}\text{O}_3\text{PS}$: C, 39.61; H, 8.07; P, 14.59.

Found: C, 39.51; H, 8.00; P, 14.79.

O,O-Diethyl-(3-ethylthio)-pentane-3-phosphonic acid ester (8b): bp 123-124°C(6.7 mmHg) as a mixture of 8b and 9b; yield 23.5%; ir (neat) 1250(P=O), 1060, 1032 and 960 cm^{-1} ; nmr (CCl_4) δ 0.98(t, 6H, $J_{\text{H-H}}=7.0\text{Hz}$, $\underline{\text{CH}_2\text{CH}_3}$), 1.21(t, 3H, $J_{\text{H-H}}=7.5\text{Hz}$, $\text{SCH}_2\underline{\text{CH}_3}$), 1.33(t, 6H, $J_{\text{H-H}}=7.0\text{Hz}$, $\text{POCH}_2\underline{\text{CH}_3}$), 1.73 and 1.88(double q, 4H, $J_{\text{H-H}}=7.0\text{Hz}$, $J_{\text{P-H}}=14\text{Hz}$, $\underline{\text{CH}_2\text{CH}_3}$), 2.78(q, 2H, $J_{\text{H-H}}=7.0\text{Hz}$, $\text{SCH}_2\underline{\text{CH}_3}$), 4.05(double q, 4H, $J_{\text{H-H}}=7.0\text{Hz}$, $J_{\text{P-H}}=8.1\text{Hz}$, $\text{POCH}_2\underline{\text{CH}_3}$)

; mass m/e 268(M⁺).

Anal. Calcd for C₁₁H₂₅O₃PS: C,46.14; H,8.80; P,10.82.

Found: C,46.24; H,8.97; P,10.71.

O,O-Diethyl-(3-mercapto)-pentane-3-phosphonic acid ester (9b): yield 29.2%; ir (neat) 2500(SH), 1245(P=O), 1060, 1025 and 965 cm⁻¹; nmr (CCl₄) δ 1.01(t,6H,J_{H-H}=7.0Hz,CH₂CH₃), 1.24(t,3H,J_{H-H}=7.5Hz,SCH₂CH₃), 1.32(t,6H,J_{H-H}=7.0Hz,POCH₂CH₃), 1.74 and 1.87(double q,4H,J_{H-H}=7.0Hz,J_{P-H}=13.5Hz,CH₂CH₃), 2.10(d,1H,J_{P-H}=5.5Hz,SH) and 4.03(double q,4H,J_{H-H}=7.0Hz,J_{P-H}=8.0Hz,POCH₂CH₃); mass m/e 240(M⁺).

Anal. Calcd for C₉H₂₁O₃PS: C,44.98; H,8.81; P,12.89.

Found: C,45.11; H,8.90; P,12.67.

O,O-Di-iso-propyl-(3-mercapto)-pentane-3-phosphonic acid ester (9c): bp 120-121°C(5.5 mmHg); yield 80%; ir (neat) 2502(SH), 1243(P=O), 1108, 1004 and 980 cm⁻¹; nmr (CCl₄) δ 1.00(t,6H,J_{H-H}=7Hz,CH₂CH₃), 1.32(d,12H,J_{H-H}=6.1Hz,POCH(CH₃)₂), 1.71 and 1.84(double q,4H,J_{H-H}=7Hz,J_{P-H}=13.4Hz,CH₂CH₃), 2.05(d,1H,J_{P-H}=6Hz,SH) and 4.63(double sep,2H,J_{H-H}=6.1Hz,J_{P-H}=7.2Hz,POCH(CH₃)₂); mass m/e 268(M⁺).

Anal. Calcd for C₁₁H₂₅O₃PS: C,46.14; H,8.80; P,10.82.

Found: C,46.29; H,9.01; P,10.57.

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CHAPTER III

REACTION OF 1,3-DITHIOLE-2-THIONES WITH TRIVALENT PHOSPHORUS COMPOUNDS

NEW SYNTHESSES OF TETRATHIAFULVALENE DERIVATIVES^{*}

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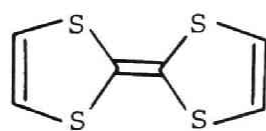
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SUMMARY

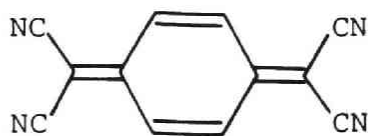
Tetracyanotetrathiafulvalene (2), tetracarbomethoxytetrathiafulvalene (6) and tetraphenyltetrathiafulvalene (8) were prepared from 4,5-disubstituted-1,3-dithiole-2-thiones in the presence of triphenyl phosphine, trialkyl- and triphenyl phosphites. This synthetic reaction is obviously explained by thiophilic attack of trivalent phosphorus compounds at the thiocarbonyl sulfur atom to form $\bar{\text{C}}\text{-S-P}^{\oplus}$ phosphoranes. By the acid hydrolyses of 2 and 6, tetraamidetetrathiafulvalene (10) and dicarboxytetrathiafulvalene (12) were newly obtained, respectively. The alkaline hydrolysis of 6 lead to the formation of tetracarbonytetrathiafulvalene (11), which was converted to bis-anhydride-tetrathiafulvalene (13) and diacid 12. Dicarbomethoxytetrathiafulvalene (14) and bis(N,N-dimethyl)amidetetrathiafulvalene (15) were also prepared from the reaction of 6 with lithium bromide in HMPA, and (N,N-dimethyl)amidetetrathiafulvalene (16) was newly prepared as monofunctionalized tetrathiafulvalene. Several new synthetic routes to parent tetrathiafulvalene from 6, 11 and 12 were established.

INTRODUCTION

The phenomenon of high electrical conductivity in the complex of tetrathiafulvalene (1,TTF) with tetracyanoquinodimethane (TCNQ)¹ has recently aroused intense interests. Several synthetic methods of tetrathiafulvalene derivatives have been studied so far: i) deproto-



TTF



TCNQ

nation of 1,3-dithiolium ions,² ii) desulfurization of 1,3-dithiole-2-thiones with trivalent phosphorus compounds, iii) pyrolysis of ortho thiooxalates,³ iv) reaction of acetylenes with carbon disulfide.⁴

Several reactions of trithiocarbonates with phosphites have been reported. Corey and Märkl⁵ have reported the reaction of 1,3-dithia-cyclohexanethione with trimethyl phosphite to give the corresponding ylide, which underwent a Wittig-type reaction with aldehydes. And Corey et al.⁶ also reported the stereospecific syntheses of olefins by the reaction of substituted ethylene trithiocarbonates with trialkyl phosphites. These reactions of trithiocarbonates could be explained to take place by initial thiophilic attack of phosphites at the thiocarbonyl sulfur atom and followed by the elimination of thiophosphate to form the carbenes, from which the olefins and ylide would be obtained. However, in the reaction of hexahydrobenzo-1,3-dithiole-2-thione with phosphite the desulfurization dimerization occurred.⁷ In this chapter, 4,5-disubstituted-1,3-dithiole-2-thiones were employed as the reactants, and the reactions with trivalent phosphorus compounds were carried out. As a result, the successful method of syntheses of tetrasubstituted tetrathiafulvalenes was established. Likewise, the formation of tetrathiafulvalenes is explained by initial thiophilic attack of trivalent phosphorus compounds at the thiocarbonyl sul-

fur atom. Using these tetrathiafulvalenes several tetrasubstituted-, disubstituted- and monosubstituted tetrathiafulvalenes were newly obtained in good yields. And several new synthetic routes to parent tetrathiafulvalene 1 (decarboxylation or decarbomethoxylation) were established.

RESULTS AND DISCUSSION

Reaction of 4,5-dicyano-1,3-dithiole-2-thione. To a boiling solution of 4,5-dicyano-1,3-dithiole-2-thione (3) in dry benzene under nitrogen was added a solution of triphenylphosphine in benzene. After several minutes the orange solid (4) began to precipitate (85%). The analytical and mass spectral data (m/e 303 (2), 294 ($S=PPh_3$)) indicate that 4 is one to one adduct of tetracyanotetrathiafulvalene and triphenylphosphine thioxide. The infrared spectrum of 4 contains, in addition to the band at 2205 cm^{-1} assigned to the cyano groups, a strong band at 1540 cm^{-1} attributable to the double bond conjugated to the cyano groups. And the difference of solubilities in several solvents (not soluble in benzene, ether; soluble in methylene chloride, acetonitrile) indicates that the solid 4 has the ionic structure (betaine). Treatment of 4 with $HB\dot{F}_4$ in methylene chloride at room temperature afforded a yellow crystalline salt, whose composition corresponded to $4+HB\dot{F}_4$ from the analytical data. The infrared spectrum of the salt exhibited the bands at 3390 and 1060 cm^{-1} , attributable to SH and BF stretching, respectively and resulting from the protonation

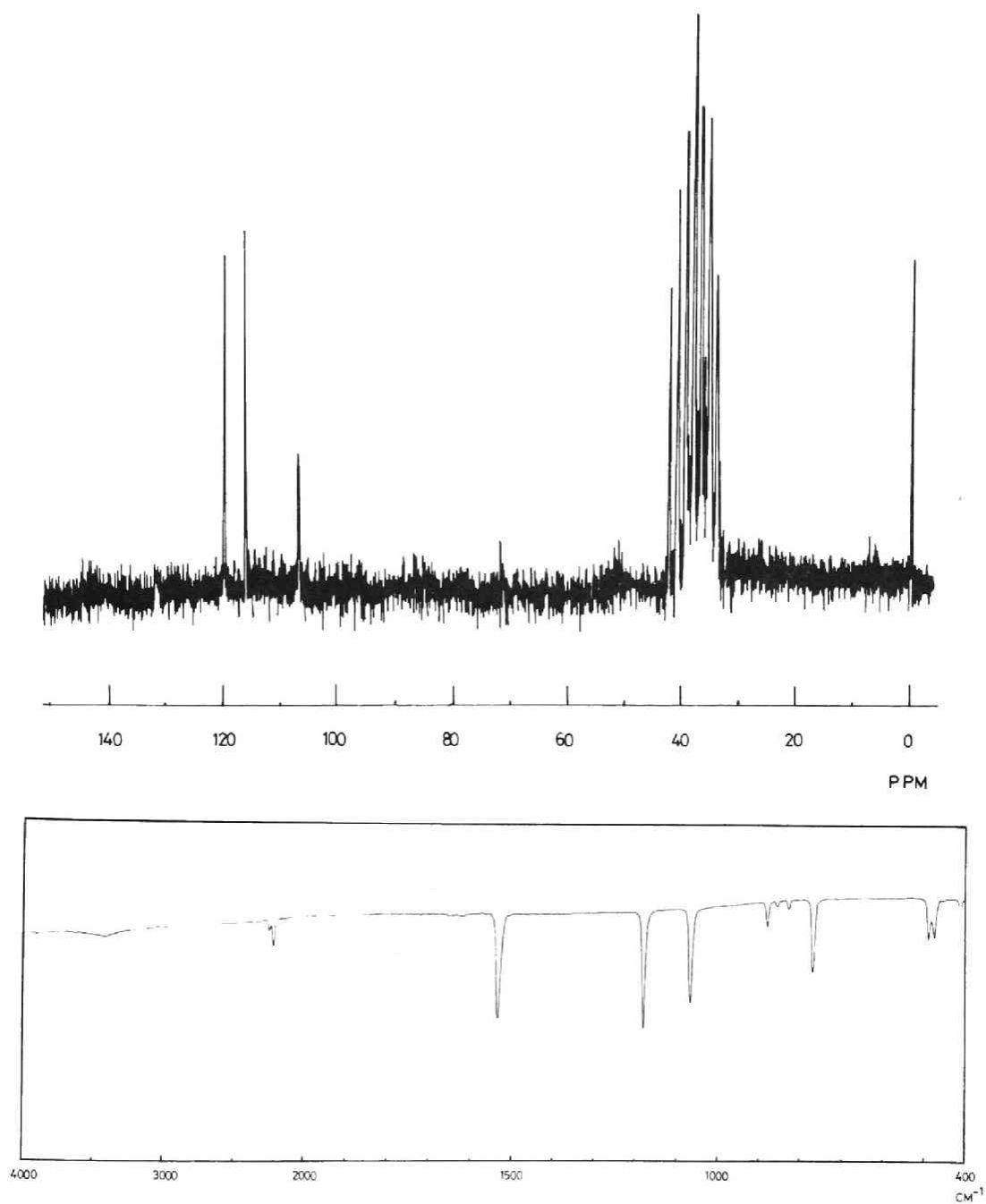


Fig. 1. ^{13}C -NMR and Infrared Spectra of Tetracyanotetrathiafulvalene (2).

of thiolate and consequent formation of normal fluoroborate salt. This adduct was also found to dissociate to 2 and triphenylphosphine thioxide by heating in dichlorobenzene. The structure of this solid might be assigned as the betaine 4.

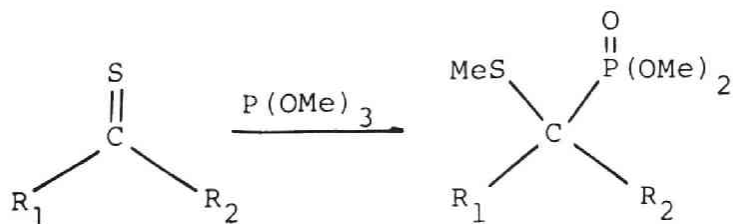
The filtrate gave the dark purple crystals (2) in 6% yield after column chromatograph on silica eluting with benzene. The structure of 2 was determined on the basis of the spectral and analytical data. The cmr and infrared spectra were illustrated in Fig 1. The infrared spectrum of 2 revealed strong bands at 2218, 1534 and 1182 cm^{-1} which are characteristic of a cyano, a carbon-carbon double bond conjugated to cyano and a C=C-S bond, respectively. And in the cmr spectrum of 2 the carbons of cyano group resonated at δ 118.9 ppm and those of carbon-carbon double bond conjugated to cyano group and central bond at δ 122.8 and 109.6 ppm, respectively. When the reaction of 3 with triphenylphosphine was carried out in toluene, similar result was obtained and the yield of 2 could not be enhanced.

On the other hand, the reactions with trialkyl phosphites were carried out in toluene at reflux temperature and found to give tetracyanotetrathiafulvalene (2) accompanying with formation of other products (for example 5). A solution of 3 and excess trimethyl phosphite in toluene was heated at reflux temperature under nitrogen for 18 hr and the reaction was monitored by thin layer chromatograph technique. After evaporation of toluene and excess trimethyl phosphite, the residue was subjected to silicagel chromatograph followed by recrystallization from methylene chloride-ether to give 2 in 12% yield.

The use of trialkyl phosphites other than trimethyl phosphite also yielded 2, but the yield was not enhanced.

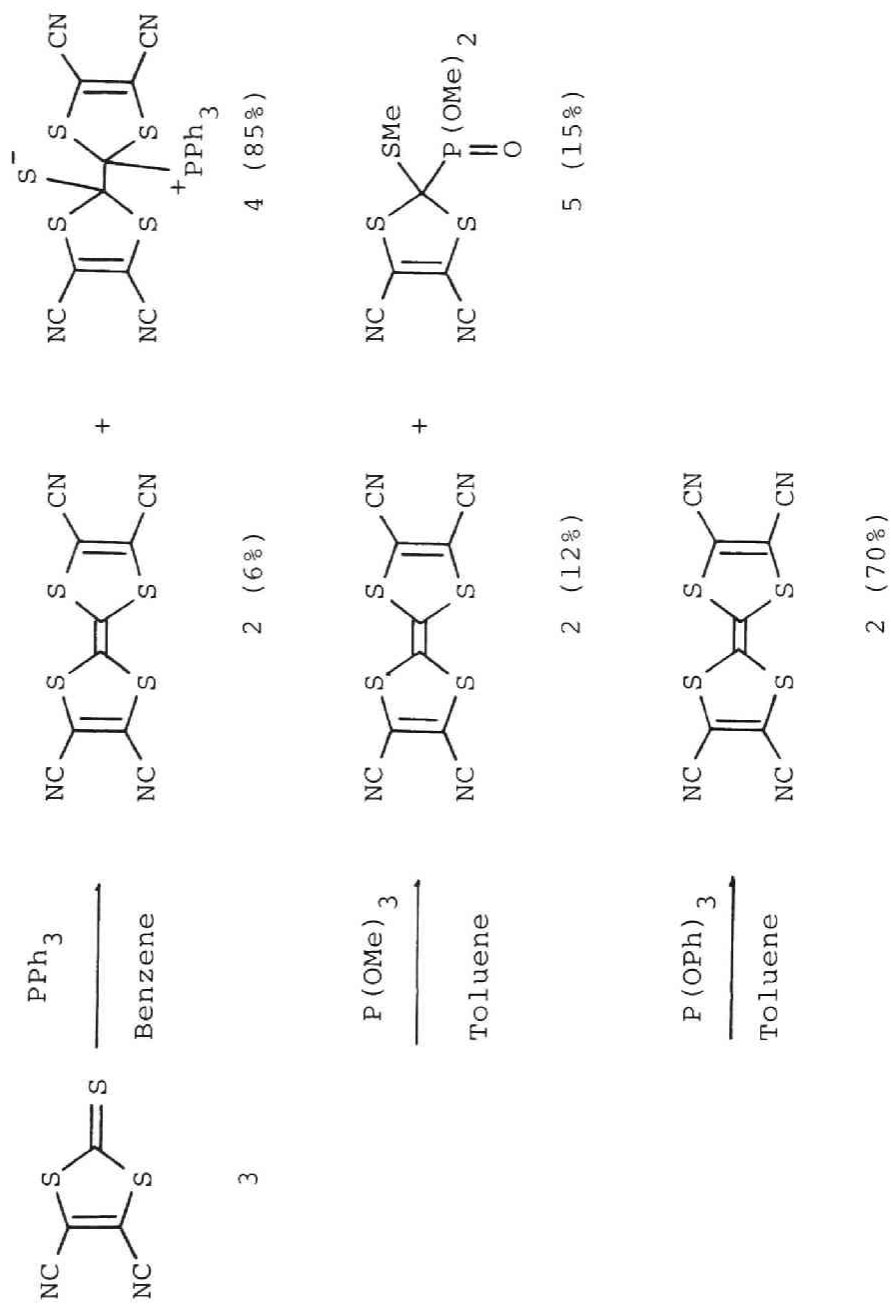
In this reaction, the pale yellow plate (5) was also isolated by chromatography. The structure of 5 was determined by its spectral and analytical data. The pmr spectrum consisted of a singlet at δ 2.75(s, 3H, SCH₃) and a doublet at δ 3.83(d, 6H, J=11.2Hz, P-O-CH₃). The infrared spectrum revealed absorptions at 2220, 1240 and 1173 cm⁻¹ which are characteristic of a cyano group, P=O double bond and P-O-Me bond, respectively. These spectral features were totally consistent with the assignment of O,O-dimethyl-4,5-dicyano-(2-methylthio)-1,3-dithiole phosphonic acid ester. The phosphonic acid ester 5 is considered to be obtained from the betaine type intermediate by the alkyl rearrangement.

In chapter I and II, alkyl rearrangement from the betaine intermediate in the reactions of aliphatic thiones with trialkyl phosphites is mentioned. Such an alkyl rearrangement should result in



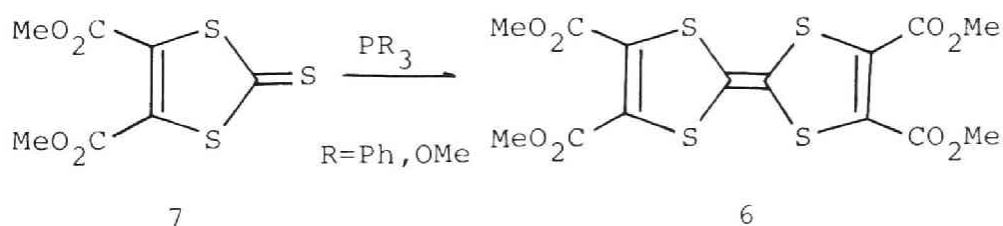
the decreased yield of 2. In accord with this consideration, the yield of 2 in the reactions of 3 with other trialkyl phosphites does not exceed 10%. However, it is known that triphenyl phosphite does

Scheme I



not undergo such an alkyl rearrangement of Arbuzov reaction.⁸ In order to inhibit the alkyl rearrangement and to enhance the yield of 2, the desulfurization of 3 with triphenyl phosphite was carried out in the same condition as in the case of the reaction with trimethyl phosphite. As expected, 2 was exclusively obtained in high yield (more than 70%) after recrystallization. These results are summarized in Scheme I.

Reaction of 4,5-dicarbomethoxy- and 4,5-diphenyl-1,3-dithiole-2-thiones. Similar desulfurization reactions of 4,5-dicarbomethoxy-1,3-dithiole-2-thione (7) with trivalent phosphorus compounds were carried out and successfully yielded tetracarbomethoxytetrathiafulvalene (6), which was firstly prepared from dimethyl acetylenedicarboxylate and carbon disulfide in the presence of acetic acid.⁹



Different from the reaction of 3, the reaction of 7 with triphenylphosphine in toluene under reflux was found to lead the exclusive formation of 6 (92%) though the reaction proceeded very slowly. After 30 hr refluxing, 60% of starting materials were recovered. In order to make the reaction proceed rapidly, xylene was used as the solvent. After refluxed 10 hr, 7 was assumed completely and the preparation of 6 in high yield (90%) was achieved. The reaction of 7

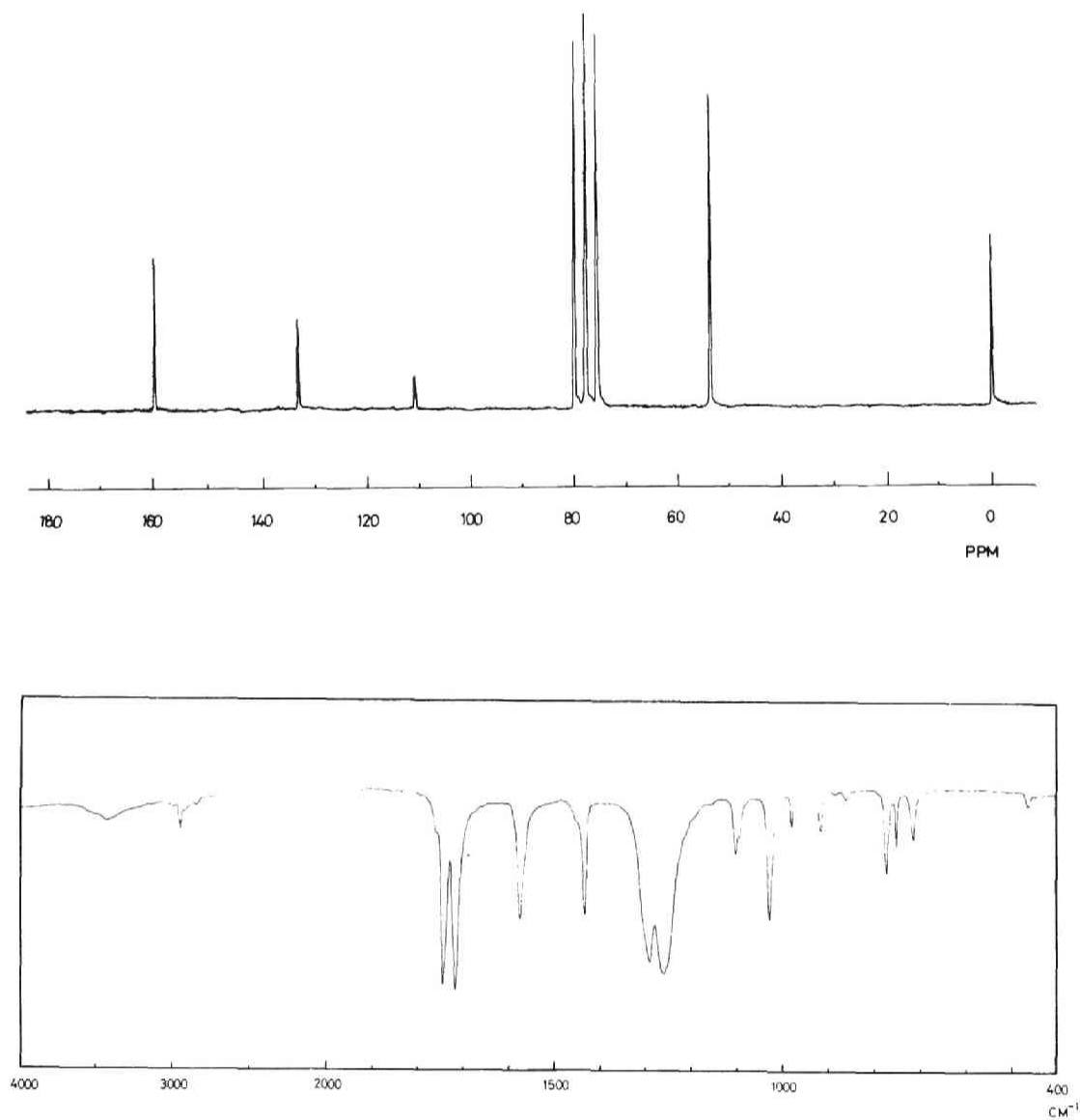
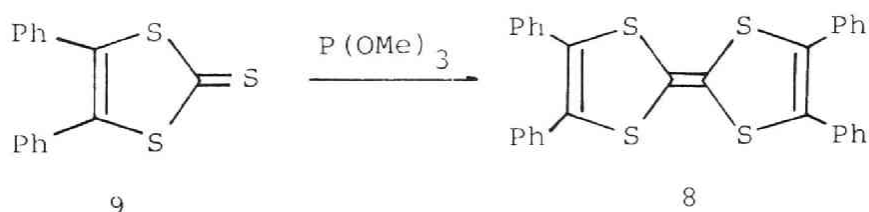


Fig. 2. ^{13}C -NMR and Infrared Spectra of Tetracarbomethoxytetrathiafulvalene (6).

with trimethyl phosphite under similar condition was also carried out. The reaction proceeded faster than with triphenylphosphine and 6 was obtained in 63% yield and several unidentified products. In order to enhance the yield of 6 by using phosphites like in the case of the reaction of 3, triphenyl phosphite was employed as a reagent. Triphenyl phosphite also reacted with 7 to give 6 in 83% yield, but the reaction proceeded too slowly, and so triphenyl phosphite is not available for the synthesis of 6.

The structure of 6 was determined on the basis of the spectral and analytical data. The infrared spectrum and cmr spectrum were illustrated in Fig 2. The infrared spectrum of 6 revealed strong bands at 1745, 1716, 1290 and 1260 cm^{-1} attributable to ester group. And in the cmr spectrum the carbons of carbonyl group resonated at δ 159.6 ppm and those of carbon-carbon double bond conjugated to carbonyl and central bond at δ 131.9 and 109.7 ppm, respectively.

Tetraphenyltetrathiafulvalene (8) was also prepared from 4,5-diphenyl-1,3-dithiole-2-thione (9) and trimethyl phosphite in 32% yield, together with several unidentified by-products.



The structure of 8 was identified with the authentic sample which was synthesized by deprotonation of 4,5-diphenyl-1,3-dithiolium

Table Desulfurization Reaction of Disubstituted
1,3-Dithiole-2-thiones

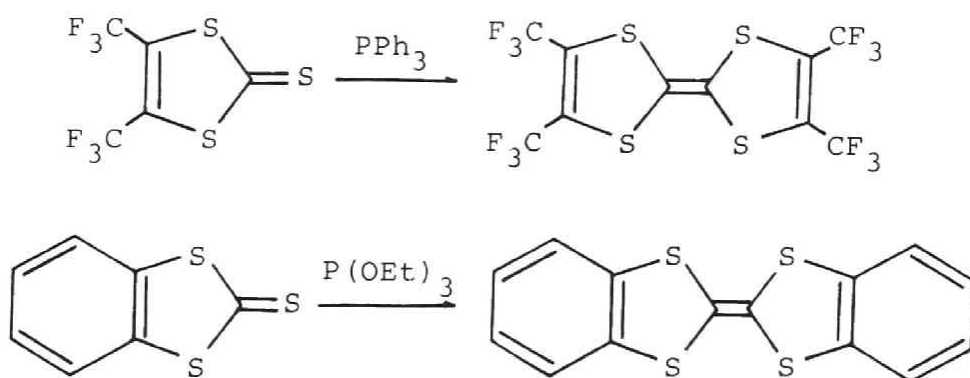


X	R	Product	Yield (%)
CN	Ph	2	6
CN	OMe	2	12
CN	OPh	2	71
CO_2Me	Ph	6	90 [*]
CO_2Me	OMe	6	63
Ph	OMe	8	32

*: when toluene is used as a solvent, 60% of starting material (7) is recovered.

salt.¹⁰ When triphenylphosphine was used as desulfurization reagent, the reaction of 9 to 8 in toluene was not observed even under reflux condition. This difference might be due to that of nucleophilicity ($\text{P(OMe)}_3 > \text{PPh}_3$). The results of the reactions of 1,3-dithiole-2-thiones with trivalent phosphorus compounds are summarized in the Table.

The synthetic studies of tetrathiafulvalene derivatives using trivalent phosphorus compounds have recently been reported by several groups. Tetrakis(trifluoromethyl)tetrathiafulvalene was synthesized by the use of triphenylphosphine from 4,5-bis(trifluoromethyl)-1,3-dithiole-2-thione¹¹ and dibenzotetrathiafulvalene* by the use of triethyl phosphite from benzo-1,3-dithiole-2-thione,^{12,13} which were also prepared from corresponding acetylenes and carbon disulfide.⁴



It is obvious from these results including the case of the re-

* The gas phase ionization potential of dibenzotetrathiafulvalene was reported to be 6.81 eV which is the same as that of TTF.¹⁴ Thus, the dibenzotetrathiafulvalene should not be classified with the others as an electron-deficient example.

actions of 3, 7 and 9 that 1,3-dithiole-2-thiones substituted by electron-withdrawing groups (CN, COOMe, Ph, CF_3 etc.) generally undergo desulfurization reaction with trivalent phosphorus compounds. However 4,5-dicarboxy- and 4,5-dicarbamide-1,3-dithiole-2-thiones did not react with triphenylphosphine and trimethyl phosphite.

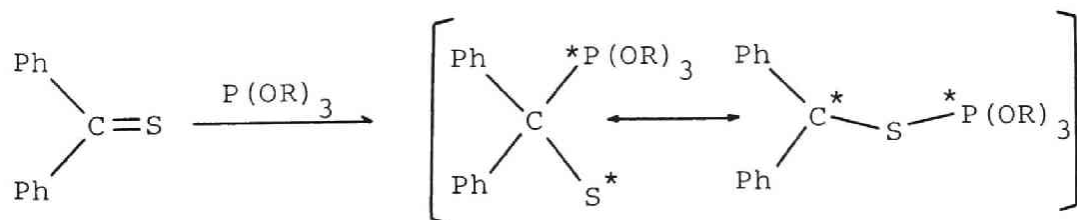
On the other hand, the reactions of 1,3-dithiole-2-thiones substituted with electron-donating groups in the presence of trivalent phosphorus compounds were carried out, but the tetrathiafulvalene derivatives were not obtained. For example, the reaction of 4,5-dimethyl-1,3-dithiole-2-thione with trimethyl phosphite in toluene at reflux temperature gave a variety of unidentified products, but no tetrathiafulvalenes.

These differences in reactivity to trivalent phosphorus compounds between 1,3-dithiole-2-thiones substituted with electron-withdrawing groups and electron-donating groups might be explained by the following consideration. In the reaction of cyclic trithiocarbonates with trialkyl phosphites, their corresponding phosphoranes were obtained, which is explained by the thiophilic attack of phosphites and following formation of carbenes. Such resulting carbenes should react with phosphites to afford phosphoranes. To the contrary, it was clearly supported by Huckel MO calculation that the canonical form of 1,3-dithiole-2-thione, shown in the following scheme, gives a large



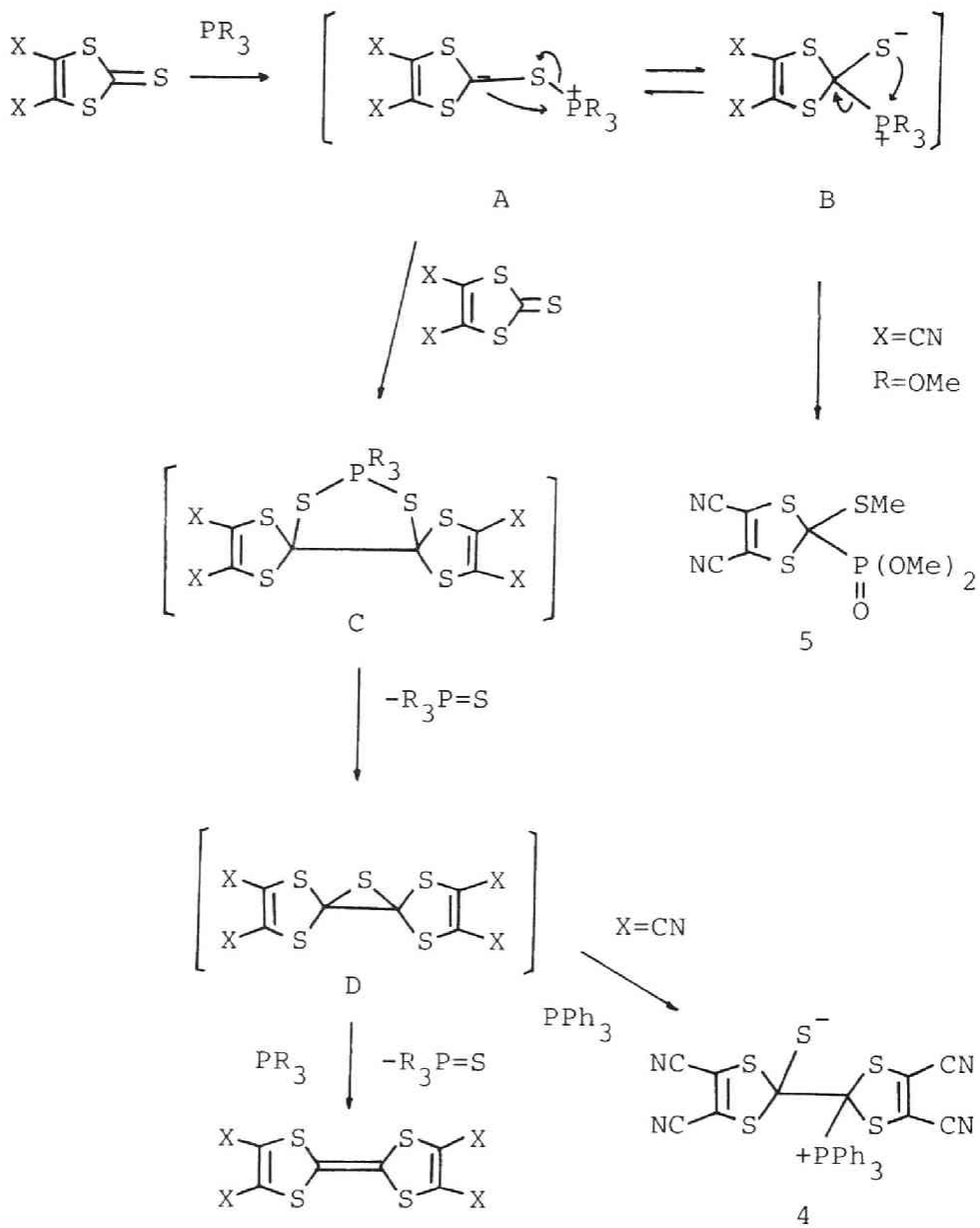
contribution in the reactions. This means that phosphites should attack to the thiocarbonyl carbon atom and afford phosphonic acid ester derivatives. Substitution with electron-withdrawing groups would lower the electron density of carbon-carbon double bond and the electronic structure of 1,3-dithiole-2-thione component would become similar to that of ethylene trithiocarbonate. Then the thiophilic attack would be preferred. On the other hand, substitution with electron-donating groups should enhance such polarization and no expected reaction may occur.

A mechanistic interpretation of the reaction of 3, 7 and 9 with trivalent phosphorus compounds is shown in Scheme II. As seen in Scheme II, initial thiophilic attack of PR_3 at the thiocarbonyl sulfur atom of 1,3-dithiole-2-thione would afford phosphorane A ($\bar{\text{C}}-\text{S}^+-\text{PR}_3$), which might isomerize to betaine intermediate B ($\text{S}^--\text{C}^+-\text{PR}_3$). Of course, the betaine intermediate B might be formed by the direct carbophilic attack of phosphite. Similar phosphorane-betaine isomerization was suggested by Ogata et al.¹⁵ in the reaction of thiobenzophenone with trialkyl phosphites. The intermediate A would react with

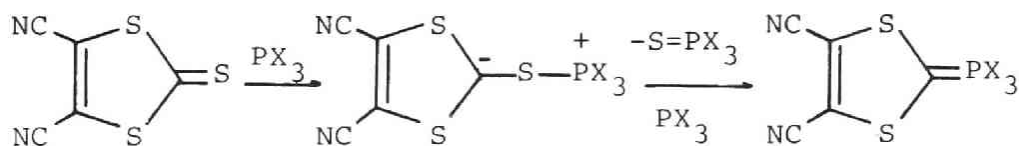


another 1,3-dithiole-2-thione to give the intermediate C containing pentavalent phosphorus atom followed by the thiirane intermediate D

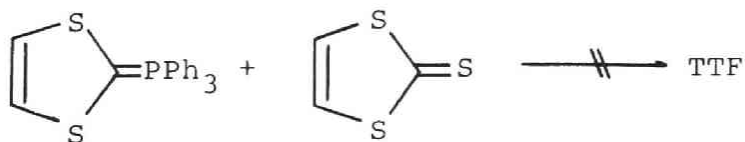
Scheme II



after dephosphine thioxide or dethiophosphate. From the intermediate D desulfurization by excess trivalent phosphorus compounds results in the formation of the tetrathiafulvalene derivatives. When triphenylphosphine was used in the reaction of 4,5-dicyano-1,3-dithiole-2-thione, triphenylphosphine would attack to the carbon atom of the thiirane ring of D to afford the betaine product 4. Similar reaction scheme via the phosphorane intermediate was mentioned by Schrowsky et al. in the reaction of benzo-1,3-dithiole-2-thione with triethyl phosphite.¹³ On the other hand, Miles et al. proposed another mecha-



nism for desulfurization via Wittig type reaction including ylide intermediate E.¹⁶ However, Cava has recently presented the experimental results that in the reaction of ylide E with 1,3-dithiole-2-thione, no tetrathiafulvalene was obtained.¹⁷ Accordingly, the benzo ylide



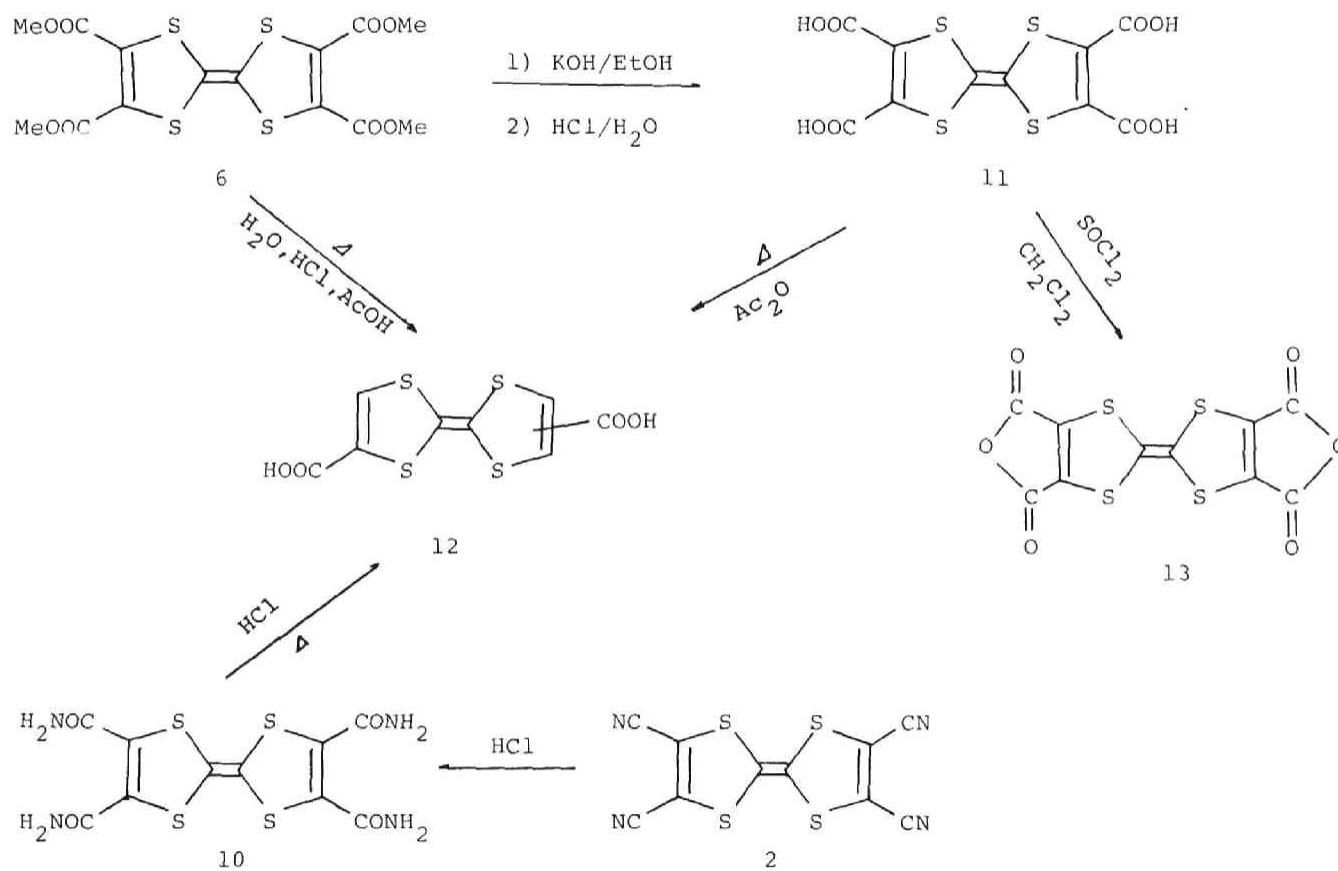
did not react with benzo-1,3-dithiole-2-thione to give dibenzotetrathiafulvalene. These findings lend more support for this mechanism

via the intermediate A than the ylide E. And when trimethyl phosphite was used in the reaction of 2, trimethyl phosphite would attack partially at the thiocarbonyl carbon atom to form the betaine B and alkyl rearrangement would afford phosphonic acid ester 5. Such rearrangement must be difficult in the reaction of 2 with triphenylphosphine and phosphite.

Reaction of some tetrathiafulvalene derivatives. Hydrolysis of tetracyanotetrathiafulvalene (2) in concentrated hydrochloric acid at room temperature afforded light purple crystallines (10) in 79% yield melting at high temperature. The structure of 10 was determined by its analytical and spectral data. The infrared spectrum of 10 revealed strong bands at 3600-2900 and 1670 cm^{-1} which are attributable to NH_2 and CONH_2 groups and is consistent with the formation of tetraamidetetrathiafulvalene. Because of insolubility of 10 the nmr spectrum could not be measured.

Hydrolysis of tetraester 6 gave two different acid derivatives depending on the reaction conditions; tetracarboxytetrathiafulvalene (11) under basic condition and dicarboxytetrathiafulvalene (12) under acidic condition, respectively. It is noteworthy that diacid 12 was directly synthesized in high yield by refluxing aqueous acetic acid solution of tetraester 6 in the presence of hydrochloric acid, since 1,3-dithiole-2-thiones substituted with carboxy groups did not react with trivalent phosphorus compounds to give tetrathiafulvalenes and moreover parent tetrathiafulvalene was directly synthesized from 12 as seen in Scheme III. In the pmr spectrum of 12, the olefin protons

Scheme III



resonated at δ 7.64 as singlet but carboxy protons disappeared owing to the H-D exchange with d^6 -DMSO. In the cmr spectrum of 12, the carbons of carboxy groups resonated at δ 160.0 ppm and those of carbon-carbon double bonds at δ 132.6 ($C=C-C=O$), 128.7 ($H-C=C$) and 110.1 ($S_2C=CS_2$) ppm. However, those data did not allow the exact assignment of the relative position of two carboxy groups.

On the other hand, refluxing ethanol solution of 6 with potassium hydroxide followed by acidification afforded light purple tetraacid 11 in quantitative yield. The reaction of tetraacid 11 with thionyl chloride in methylene chloride afforded bis-anhydride-tetrathiafulvalene (13) quantitatively, whose structure was determined by its infrared spectrum, absorptions at 1850 and 1870 cm^{-1} characteristic for unsaturated five-membered anhydride and its analytical data. Usually such anhydrides are prepared by the reaction of cis-diacid with acetic anhydride, but an attempt to prepare 13 in the same way resulted in the formation of diacid 12 in good yield, in connection with which the decarboxylation of tetraacid 11 has been reported not to be attained in basic solvent as pyridine.¹⁸

The parent tetrathiafulvalene is wellknown to be easily air-oxidized,¹⁹ whilst the tetrathiafulvalenes obtained in this work (2, 6, 8 and 10-16) are very stable against air oxidation, which is consistent with the calculated results by Huckel MO method that the energy levels of highest occupied molecular orbitals of those derivatives are quite low comparing with that of parent TTF.

New synthetic routes to parent tetrathiafulvalene. Although parent

tetrathiafulvalene was firstly prepared by deprotonation of 1,3-dithiolium cation,² the Du Pont group's synthesis is by far best method for preparing large amount of tetrathiafulvalene,²⁰ and the procedure of Wudl et al. is easy to carry out for smaller scale reactions,²¹ several attempts to prepare TTF (1) by utilizing the facile preparation of tetracarbomethoxy- (6), tetracarboxy- (11) and dicarboxytetrathiafulvalene (12) were carried out.

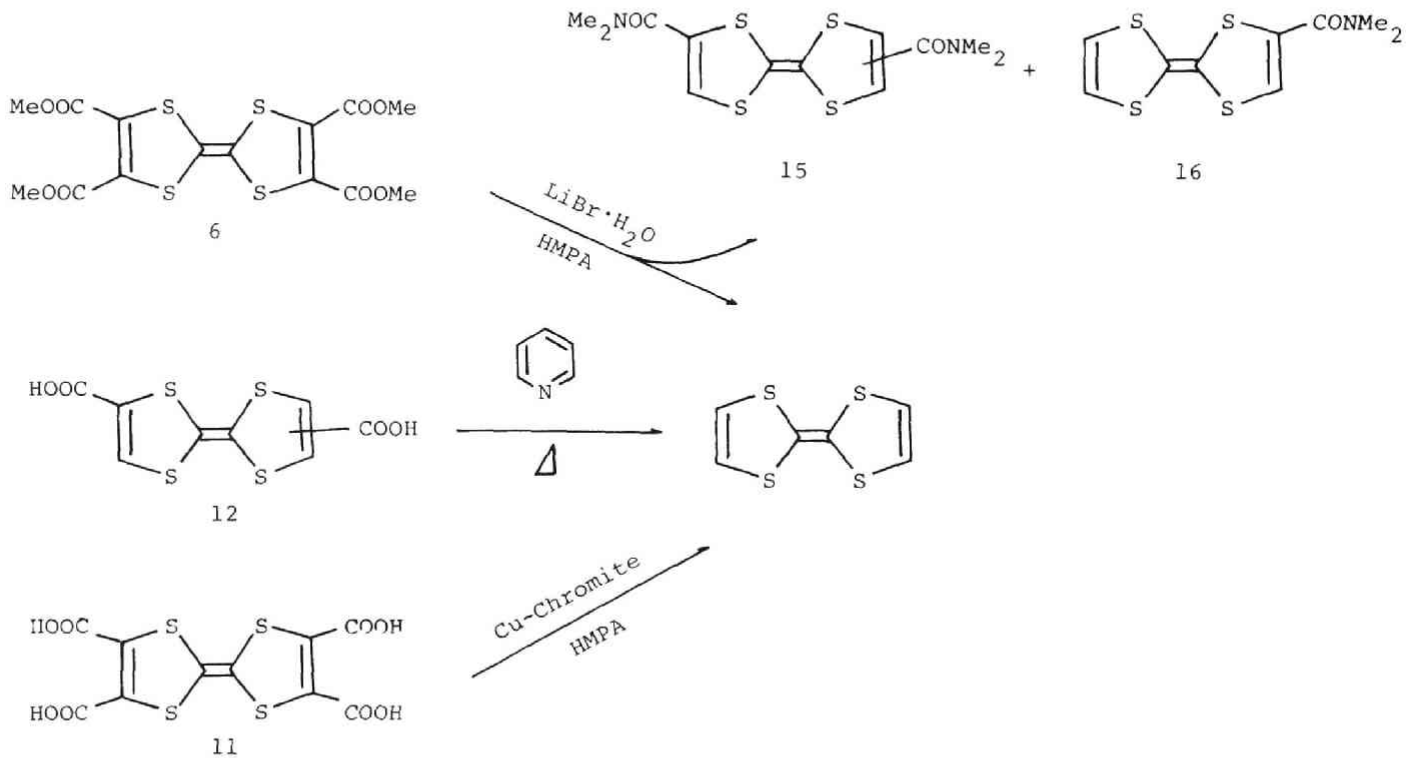
A mixture of tetraester 6 and excess lithium bromide mono hydrate in HMPA was gradually heated to 80°C and the temperature was maintained for 2 hr, during this time the color of the mixture turned to orange red and the gas evolution was observed. When the heating was stopped at this time and the mixture was treated with deaerated water, a mixture of TTF and dicarbomethoxytetrathiafulvalene (14) was obtained in 11% and 53% yields, respectively. The structure of 14 was determined by comparing its spectral data with the literature.^{18,20} After gas evolution ceased, the temperature was elevated to 150-160°C for 10 min and the mixture was treated with water to precipitate orange solids, which were subjected to chromatograph on silica to afford TTF (1; 13%), bis(N,N-dimethyl)-carbamidetetrathiafulvalen (15; 22.3%) and (N,N-dimethyl)-carbamidetetrathiafulvalene (16; 18.5%). The structures of 15 and 16 were determined by their analytical and spectral data. In the pmr spectrum of 15 the methyl protons attached to nitrogen atom and olefin protons appeared as two singlets at δ 3.10 and 6.63, respectively. Generally the methyl protons attached to nitrogen atom of amide group appear as a doublet because of the

canonical resonance. In the spectrum of 15, such phenomenon was not observed, which indicates that tetrathiafulvalene component is more electron-donating than amino group. Furthermore, in the pmr spectrum of 16 the methyl and olefin protons appeared as three kinds of singlets at δ 3.09, 6.34 and 6.61 ppm. The chemical shift of olefin protons on the side of unsubstituted ring is quite similar to that of parent TTF and the methyl protons appeared as a singlet, which indicate that only substituted side of electron rich component is donating to carbamide group. Accordingly, though tetra and disubstituted tetrathiafulvalenes have been reported so far, 16 is the first monofunctionalized tetrathiafulvalene. Such method of removing carbomethoxy substituents was also reported in the preparation of tetraselenafulvalene.²²

The decarboxylation of acid derivatives gave also parent TTF. Tetraacid 11 was heated with Copper-Chromite in HMPA at 150°C for 3 hr and the reaction mixture was treated with water. The benzene extracts upon evaporation gave a 57% yield of tetrathiafulvalene. This route is more available than the one mentioned above because of easy handling and no by-products. Without Copper-Chromite, 12 was recovered quantitatively.

Also the preparation of parent TTF by combining the facile preparation of 12 and the decarboxylation of 12 by Hartzler et al.²⁰ was carried out. This route including only three steps (3→2→12→TTF) provides a new synthetic route to TTF with a total yield of 53% yield based on 4,5-dicarbomethoxy-1,3-dithiole-2-thione. Scheme IV shows

Scheme IV



the new synthetic routes to parent TTF.

EXPERIMENTAL

Melting points were determined using a Buchi melting point apparatus in sealed capillary tubes and are uncorrected. The electronic absorption spectra were measured on a Hitachi ESP-3T recording photometer, the infrared spectra were determined on Hitachi grating ir spectrophotometer, Model 215, the mass spectra were determined on Hitachi RMU-6C or RMS-4 mass spectrometer, the pmr spectra were recorded on a Varian HA-100 spectrometer and the cmr spectra were recorded on JEOL FX-60 spectrometer. Elemental analyses were carried out at the Elemental Analytical Center of Kyoto University.

4,5-Dicyano-1,3-dithiole-2-thione (3) was prepared as described by Klingsberg,²³ and 4,5-dicarbomethoxy-1,3-dithiole-2-thione (7) was prepared as described by O'Connor et al.²⁴ and 4,5-diphenyl-1,3-dithiole-2-thione (9) was prepared from 4,5-diphenyl-1,3-dithiolium ion with sodium hydrogen sulfide. The phosphine and phosphites were commercial materials and were used as received. Kieselgel 60 F₂₅₄ (Merck) was used for thin layer chromatography. Wakogel C-200 was used for the absorbent of column chromatography.

Reaction of 3 with Triphenylphosphine. To a boiling solution of 3 (0.200g) in 15 ml of dry benzene under nitrogen was added a solution of triphenylphosphine (0.450g) in 10 ml of benzene. After several minutes the orange solid began to precipitate. The resulting solid

was filtered, washed with cool benzene and recrystallized from methylene chloride-ether to give 0.270g of orange crystals (4); yield 85%; mp 169-172°C (dec.); ir (KBr) 2210, 2170(CN), 1540(C=C) and 1415 cm^{-1} ; mass m/e 304, 294(S=PPh₃).

Anal. Calcd for C₂₈H₁₅N₄PS₄: C,56.17; H,2.53; N,9.36.

Found: C,56.27; H,2.56; N,9.42.

The filtrate was concentrated and column chromatographed on silica. The red band upon evaporation gave 0.018g of dark purple needles after recrystallization from methylene chloride-ether (2); yield 6%; mp 264-265°C (dec.); ir (KBr) 2208(CN), 1534(C=C), 1182 and 1066 cm^{-1} ; cmr (d₆-DMSO) δ 109.6(S₂C=CS₂), 118.9(CN) and 122.8(=C-CN) ppm; mass m/e 304(M⁺).

Anal. Calcd for C₁₀N₄S₄: C,39.46; N,18.41; S,42.14.

Found: C,39.04; N,18.34; S,42.37.

Reaction of 3 with Trimethyl Phosphite. A mixture of 1.00g of 3 and 1.50 g of trimethyl phosphite in 50 ml of toluene was heated under reflux for 6 hr under nitrogen. The resulting dark solution was concentrated and chromatographed on silica eluting with benzene. The yellow band upon evaporation gave 0.117g of yellow crystals (5); yield 15%; mp 140-141°C; ir (KBr) 2220(CN), 1547(C=C), 1240(P=O), 1180 (P-O-Me) and 1054-1012 cm^{-1} ; pmr (CDCl₃) δ 2.75(s,3H,SCH₃) and 3.83(d,6H,J=11.2Hz,P-O-CH₃).

Anal. Calcd for C₈H₉N₂O₃PS₃: C,31.16; H,2.94; N,9.09; P,10.05.

Found: C,31.32; H,2.70; N,9.11; P,10.31.

In this reaction, 2 was obtained in 12 % yield.

Reaction of 3 with Triphenyl Phosphite. A mixture of 1.008g of 3 and 15 ml of triphenyl phosphite in 50 ml of toluene was heated under reflux overnight and concentrated. The dark residue was subjected to chromatography on silica eluting with benzene. The red band upon evaporation gave 0.603g (70%) of dark purple crystals (2).

$\Delta^{2,2'}$ -Bis(4,5-dicarbomethoxy-1,3-dithiolidene) (6).

A. A mixture of 0.250g of 7 and 0.416g of triphenylphosphine in 20 ml of toluene was heated under reflux for 30 hr. The red solution was concentrated and chromatographed on silica eluting with chloroform. The initial colorless band contained triphenylphosphine and triphenylphosphine thioxide. The yellow band led to recovery of 0.150 g of 7. The subsequent red band upon evaporation gave 0.082g of brown crystals (6); yield 92%; mp 168-169°C (lit. 169-170°C); ir (KBr) 1745, 1716(C=O), 1576(C=C), 1290 and 1260(C-O-CH₃) cm⁻¹; pmr (CDCl₃) δ 3.83(s); cmr (CDCl₃) δ 53.4(OCH₃), 109.7(S₂C=CS₂), 131.9(=C-C=O), 159.6(C=O) ppm; mass m/e 436(M⁺).

Anal. Calcd for C₁₄H₁₂O₈S₄: C, 38.52; H, 2.77; O, 29.32.

Found: C, 38.54; H, 2.94; O, 29.57.

B. A mixture of 0.506g of 7 and 1.00g of trimethyl phosphite in 30 ml of toluene was allowed to reflux for 10 hr. A dark residue after concentration was chromatographed on silica to give 0.222g (62%) of 6.

C. A mixture of 0.250g of 7 and 0.530g of triphenylphosphine in 10 ml of xylene was heated under reflux for 10 hr. A dark residue after evaporation of solvent was chromatographed on silica to give

0.195g (90%) of 6.

$\Delta^{2,2'}$ -Bis(4,5-diphenyl-1,3-dithiolidene) (8). A mixture of 0.286g of 9, 0.5 ml of trimethyl phosphite and 10 ml of toluene was heated under reflux under nitrogen for 24 hr. The red solution was evaporated and the residue was recrystallized from acetonitrile to give 0.083g (32%) of orange crystals (8); mp 261.5-263°C (lit. 262-263°C). Spectral data were all identical with authentic sample.

$\Delta^{2,2'}$ -Bis(4,5-dicarbamide-1,3-dithiolidene) (10). A mixture of 76mg of finely ground 2 and 10 ml of concentrated hydrochloric acid was allowed to stand for two weeks at room temperature under stirring. The solid was filtered and washed with water and with ethanol. After dried, 74mg of purple solids were obtained (10); yield 79%; mp > 360°C; ir (KBr) 3600-2900(N-H), 1670(C=O) and 1390-70 cm^{-1} ; uv-vis (DMF) λ_{max} (log ϵ) 449(3.31) and 319 nm(4.18); mass m/e 376(M^+).

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{N}_4\text{O}_4\text{S}_4$: C, 31.90; H, 2.14; N, 14.88; O, 17.00. Found: C, 31.67; H, 2.29; N, 14.57; O, 17.10.

$\Delta^{2,2'}$ -Bis(4,5-dicarboxy-1,3-dithiolidene) (11). A mixture of 0.637g of 6, 1.0g of potassium hydroxide and 40 ml of ethanol was heated under reflux for 1 hr. The resulting orange-yellow potassium salts were filtered and dissolved in 15 ml of water. Neutralization with hydrochloric acid yielded purple solids. These were filtered and dried without washing, because of water solubility. Recrystallization from DMF-ether gave 0.590g of light purple crystals (11); yield 100%; mp > 360°C; ir (KBr) 3600-2700(O-H), 1550(C=O), 1503(C=C) and 1360(C-O) cm^{-1} ; cmr (d_6 -DMSO) δ 103.8($\text{S}_2\text{C}=\text{CS}_2$), 139.1($=\text{C}-\text{C}=\text{O}$), 160.5 and 162.2

(C=O) ppm; uv-vis (DMF) λ_{\max} (log ϵ) 477(3.33), 311(4.17) and 302nm(4.10).

Anal. Calcd for $C_{14}H_4O_8S_4$: C, 39.25; H, 9.41; O, 29.88.

Found: C, 39.21; H, 9.56; O, 29.97.

$\Delta^{2,2'}$ -Bis(4(5)-carboxy-1,3-dithiolidene) (12).

A. 63 mg of 11 was suspended in 5 ml of acetic anhydride and heated under reflux for 0.5 hr. Red crystals precipitated and filtered and dried to give 36 mg of 12; yield 76%; mp > 360°C; ir (KBr) 3400-3200(O-H), 1650(C=O), 1540(C=C), 1425 and 1295(C-O) cm^{-1} ; pmr (d_6 -DMSO) δ 7.64(s, =C-H); cmr (d_6 -DMSO) δ 110.1($S_2C=CS_2$), 128.7(C=C-H), 132.6(=C-C=O) and 160.0(C=O) ppm.

Anal. Calcd for $C_8H_4O_4S_4$: C, 32.86; H, 1.38; O, 21.89.

Found: C, 32.84; H, 1.49; O, 22.08.

B. A mixture of 0.400g of 6, 18 ml of water, 18 ml of concentrated hydrochloric acid and 50 ml of glacial acetic acid was heated under reflux for 3 hr. The resulting solid was filtered and dried, yielded 0.250 g (92%) of red crystals 12.

$\Delta^{2,2'}$ -Bis(4,5-dicarboxy anhydride-1,3-dithiolidene) (13). A mixture of 60 mg of 11, 0.5 ml of thionyl chloride and 3 ml of methylene chloride was heated under reflux for 1 hr. The dark solution was evaporated to give the dark residue, which was crystallized from n-hexane to give 53 mg of dark brown needles (13); yield 100%; ir (KBr) 1850, 1780(C=O for unsaturated five-membered anhydride), 1560(C=C) and 1255 cm^{-1} ; mass m/e 344(M^+).

Anal. Calcd for $C_{10}O_6S_4$: C, 34.88; O, 27.88.

Found: C, 35.01; O, 27.92.

Reaction of 6 with Lithium Bromide. (New Synthetic Route to TTF, 1)

A mixture of 436 mg of 6, 3g of lithium bromide monohydrate and 10 ml of hexamethylphosphoramide was heated gradually to 80°C. There was gas evolution and considerable lightening of color. When gas evolution ceased, the mixture was cooled and treated with deaerated water to give the red solids. After filtration, the solid was subjected to column chromatography on silica. The first yellow fraction upon evaporation gave 22 mg of 1; yield 11%; mp 107-109°C (lit. 109.0-109.5°C); pmr (CDCl₃) δ 6.33 (s, =C-H) (lit. 6.32); mass m/e 204(M⁺).

The second red band upon evaporation gave dicarbomethoxytetrathiafulvalene (166 mg) (14); yield 53%; mp 226-228°C (dec.) (lit. 242-244°C); pmr (CDCl₃) δ 3.85(s, 6H, OCH₃) and 7.30(s, 2H, =C-H); ir (KBr) 1708(C=O), 1548(C=C), 1440 and 1255(C-O) cm⁻¹; mass 320(M⁺).

Anal. Calcd for C₁₀H₈O₄S₄: C, 37.48; H, 2.52; O, 19.97.

Found: C, 37.45; H, 2.64; O, 20.09.

When gas evolution ceased, the temperature was raised to 150-160°C for 10 min. The cooled mixture was diluted with water and extracted with benzene. The orange organic extract was washed, dried over Na₂SO₄, and after concentration subjected to chromatography on silica eluting with methylene chloride. The first yellow band upon evaporation gave 27 mg of orange-yellow crystals 1; yield 13%. The second yellow fraction gave 51 mg of (N,N-dimethyl)carbamidetetrathiafulvalene (16); yield 18.5%; mp 162.5-163.5°C; ir (KBr) 3050(C=C-H), 1603(C=O), 1580, 1540(C=C) and 1395 cm⁻¹; pmr (CDCl₃) δ 3.09(s, 6H,

N-CH₃), 6.34(s, 2H, H-C=C-H) and 6.61(s, 1H, H-C=C-C=O); mass m/e 275(M⁺).

Anal. Calcd for C₉H₉NOS₄: C, 39.25; H, 3.29; N, 5.09; S, 46.57.

Found: C, 39.46; H, 3.02; N, 5.06; S, 46.44.

The third orange-red band upon evaporation after recrystallization from methylene chloride-ether yielded 77 mg of orange bis(N,N-dimethyl)carbamidetetrathiafulvalene (15); yield 22.3%; mp 231-232°C; ir (KBr) 3090, 1602(C=O), 1550(C=C) and 1400 cm⁻¹; pmr (CDCl₃) δ 3.10(s, 12H, N-CH₃) and 6.63(s, 2H, H-C=C-C=O); mass m/e 346(M⁺).

Anal. Calcd for C₁₂H₁₄N₂O₂S₄: C, 41.59; H, 4.07; S, 37.01; N, 8.08.

Found: C, 41.58; H, 3.80; S, 37.00; N, 8.05.

Decarboxylation of 11 with Copper Chromite. A mixture of 760 mg of 11, 300 mg of Copper Chromite and 15 ml of HMPA was heated to 150-160°C for 3 hr. The cooled mixture was diluted with water and extracted with benzene. The yellow organic extract was washed, dried over Na₂SO₄ and evaporated to yield orange-yellow crystals, which were recrystallized from hot hexane to give orange needles 1 (231 mg); yield 57%. Other by-products were not observed.

Decarboxylation of 12. A mixture of 141 mg of 12 and 4 ml of pyridine was sealed in a heavy wall glass tube under argon. The tube was heated at 250°C for 1.5 hr. After cooling, the solvent was evaporated under reduced pressure. The dark residue was extracted with three 10 ml portions of acetonitrile. The extracts were evaporated and the residue was sublimed at 110°C (0.3 mmHg) to give 63 mg of orange product (63%). The structure was identified by pmr spectrum.

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CHAPTER IV

ELECTRONIC STRUCTURE AND INTRAMOLECULAR CHARGE-TRANSFER ABSORPTION SPECTRA OF TETRACYANOTETRATHIAFULVALENE

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Submitted to Tetrahedron.

SUMMARY

Electronic spectrum of tetracyanotetrathiafulvalene was measured in uv-vis regions and interpreted with the aid of ASMO-SCF-CI method. The theoretical treatment showed that the absorption band at the longest wave length is interpreted in terms of the intramolecular charge-transfer.

INTRODUCTION

In the preceeding chapter III, tetracyanotetrathiafulvalene (1) was prepared by the reaction of 4,5-dicyano-1,3-dithiole-2-thione with trivalent phosphorus compounds. The compound 1 has both the electron-donating moiety (central electron-rich olefin component) and the electron-accepting moiety (dicyano ethylene component) within a molecule.

An absorption band characteristic of a molecular compound between electron donor and acceptor was interpreted as a transition between two levels caused by resonance of no-bond and dative structures, with an electron transferred from donor to acceptor and a covalent bond formed between them in the dative structure, and was called as an intermolecular charge-transfer absorption band.¹ It seems reasonable to expect that a similar phenomenon occurs in a molecule which is composed of electron-donating and -accepting groups. When an electron donating group and an electron accepting group com-

bine with each other through a bridge of conjugated double bonds or hetero atoms, so that π -electrons are able to migrate from the former to the latter, it may be expected that the system gives rise to a special absorption band inherent to neither of the components. By analogy with the case of molecular compounds, it is called an intramolecular charge-transfer band.²

Theoretical treatment of 1 by ASMO-SCF-CI method showed that the electronic absorption band at the longest wave length is reasonably interpreted in terms of the intramolecular charge-transfer.

EXPERIMENTAL

The compound, 1, was prepared by the reaction of 4,5-dicyano-1,3-dithiole-2-thione with triphenyl phosphite; mp 264-265°C(dec.). The electronic spectra of 1 were recorded on a Hitachi EPS-3T spectrophotometer in benzene and in methanol between 210 and 700 nm. The observed spectra were analyzed by assuming that the absorption bands are approximated by Gaussian curves, thus three peaks were obtained. Observed absorption bands and molecular extinction coefficients are presented in Table 1.

Table 1. Electronic Spectrum of Tetracyanotetrathiafulvalene

Solvent	λ_{\max} (nm)	($\log \epsilon_{\max}$)	Solvent	λ_{\max} (nm)	($\log \epsilon_{\max}$)
benzene	502	(3.30)	methanol	480	(3.39)
	328	(4.18)		320	(4.04)
	—			260	(4.20)

CALCULATION

The calculations were carried out using the general basic approximations; (i) the zero-differential overlap approximation except for the one-center exchange integrals, (ii) the I - E approximation for the one-center Coulomb integrals, (iii) the Ohno approximation for the one-center and two-center Coulomb repulsion integrals. Under these approximations, the best ground state molecular orbitals were obtained by the self-consistent field method.

The molecular orbital (ϕ_i) is expressed as a linear combination of all the valence atomic orbitals (χ_r) centered on the atoms of a molecule,

$$\phi_i = \sum_r C_{ir} \chi_r \quad (1)$$

where the coefficients are the solutions of Roothaan equation.³

Introducing the zero-differential overlap approximation, except for the one-center exchange integrals, the diagonal elements of the Fock's operator for a closed-shell molecule are given by:

$$F_{rr} = H_{rr} + \frac{1}{2} P_{rr} (rr|rr) + \sum_{r'}^{\text{on } A} P_{r'r'} [(rr|r'r') - \frac{1}{2}(rr'|rr')] \\ + \sum_B \sum_s^{\text{on } B} P_{ss} (rr|ss) \quad (2)$$

where $(rr|ss)$ and $(rr'|rr')$ are the two-center Coulomb and one-center exchange repulsion integrals, respectively; where $\sum_{r'}^{\text{on } A}$ denotes the summation over all the valence atomic orbitals of the A atom except

for the r th atomic orbital, and where the diagonal core integrals, H_{rr} , are given as follows;

$$H_{rr} = U_{rr} + \sum_B (B|rr) \quad (3)$$

$$U_{rr} = -I_r - (N_r - 1)(rr|rr) - \sum_{r'}^{\text{on } A} N_{r'} [(rr|r'r') - \frac{1}{2}(rr'|rr')] \quad (4)$$

$$(B|rr) = - \sum_s^{\text{on } B} N_s (ss|rr) \quad (5)$$

where I_r is the valence state ionization potential of the r th atomic orbital and where N_r denotes the number of the valence electrons occupying the r th atomic orbital. For the valence p atomic orbital, U_{rr} is taken as the average value for the p_x, p_y and p_z atomic orbitals on the same atom.

The off-diagonal elements of the Fock's operator are expressed in either of two ways, according to whether they are concerned with one- or two-centers;

$$F_{rr'} = -\frac{1}{2} P_{rr'} [(rr|r'r') - 3(rr'|rr')] \quad (6)$$

($r \neq r'$, both on the same atom)

$$F_{rs} = H_{rs} - \frac{1}{2} P_{rs} (rr|ss) \quad (7)$$

($r \neq s$, on different atoms)

where H_{rs} is the core resonance integral, which is given by the following two equations;

$$H_{rs} = -\frac{1}{2} K S_{rs} (I_r + I_s) \quad (8)$$

($r \neq s$, adjacent atoms)

$$H_{rs} = 0 \quad (r \neq s, \text{ otherwise}) \quad (9)$$

where S_{rs} is the overlap integral between the r th and the s th atomic orbitals and where K is a constant taken to be 0.8 in the present calculation. The overlap integrals are calculated with the Slater-type atomic orbitals, where the exponent values are those obtained by Clementi and Raimondi.⁴

The one center Coulomb repulsion integrals are approximated as follows;

$$(rr|rr) = I_r - E_r \quad (10)$$

where E_r is the valence state electron affinity of the r th atomic orbital. The one-center and two-center Coulomb repulsion integrals are calculated by the Ohno approximation:

$$(rr|ss) = \frac{1}{2} \left(\sqrt{1/R_{rs}^2 + 1/(rr|rr)^2} + \sqrt{1/R_{rs}^2 + 1/(ss|ss)^2} \right) \quad (11)$$

where R_{rs} is the distance between the atoms to which the two atomic orbitals belong.

The one-center exchange integrals are evaluated by the Slater-Condon parameters estimated by Hinze and Jaffe.⁵ These values used are listed in Table 2, together with the values of I_r and $(rr|rr)$.

An initial set of molecular orbital coefficients is obtained by putting F_{rr} as equal to $-I_r$ and by reducing F_{rs} to the H_{rs} term only. The iteration procedure is carried out until the variation in every molecular orbital energy remains within 0.001 eV.

For the electronic transitions, 36 kinds of low-lying singlet-singlet one electron excitations were considered and the configuration

Table 2. Slater Exponents (ζ_r) and Valence State Ionization Potentials (I_r) of Atomic Orbitals and Electron Repulsion Integrals

		$\zeta_r^{a)}$	$I_r, \text{ eV}^{b)}$	$(rr rr), \text{ eV}^{c)}$	$(rr' rr'), \text{ eV}^{d)}$
C	2s	1.6083	-20.01	12.10	$(2s2p 2s2p) = 2.30$
	2p	1.5679	-11.27	10.93	$(2p2p' 2p2p') = 0.54$
N	2s	1.9237	-26.92	12.87	$(2s2p 2s2p) = 2.99$
	2p	1.9170	-14.42	11.88	$(2p2p' 2p2p') = 0.77$
S	3s	2.1223	-20.08	8.54	$(3s3p 3s3p) = 1.02$
	3p	1.8273	-13.32	9.82	$(3p3p' 3p3p') = 0.55$
	3d	0.8400	-3.67	5.90	

a) E. Clementi and D. L. Raimondi, J. Chem. Phys., 38, 2686 (1963).

b) J. Hinze and H. H. Jaffé, J. Am. Chem. Soc., 84, 540 (1962).

c) $(rr|rr) = I_r - E_r$

d) J. Hinze and H. H. Jaffé, J. Chem. Phys., 38, 1834 (1963).

interaction among these excited states were carried out. Let $V_{(i \rightarrow j)}$ be the determinantal wave function in which one electron is excited from an occupied molecular orbital ϕ_i to a vacant molecular orbital ϕ_j with spin antiparallel, then the excitation energy can be written using SCF-MO energy,

$$\Delta E_{(i \rightarrow j)} = \epsilon_j - \epsilon_i - J_{ij} + 2K_{ij} \quad (12)$$

where J_{ij} and K_{ij} are molecular Coulomb integrals and molecular exchange integrals, respectively,

$$J_{ij} = \iint \phi_i^*(1)\phi_i(1) \frac{1}{r_{12}} \phi_j^*(2)\phi_j(2) dv(1)dv(2) \quad (13)$$

$$K_{ij} = \iint \phi_i^*(1)\phi_j(1) \frac{1}{r_{12}} \phi_i^*(2)\phi_j(2) dv(1)dv(2) \quad (14)$$

The excited state of the molecule is expressed as a linear combination of singly excited state configurations after the configuration interaction.

$$\phi_{\text{exc}} = \sum_{i,k} C_{ik} V_{(i \rightarrow k)} \quad (15)$$

The coefficients C_{ik} and the singlet-singlet excitation energies are obtained by diagonalizing configuration interaction matrixes with the element given by

$$[V_{(i \rightarrow j)} | H | V_{(k \rightarrow l)}] = 2[jl | ki] - [ji | kl] \quad (16)$$

$$[ij | kl] = \iint \phi_i^*(1)\phi_j(1) \frac{1}{r_{12}} \phi_k^*(2)\phi_l(2) dv(1)dv(2) \quad (17)$$

The entire procedure was programmed and run on a Facom 230-60 computer.

Structural model for 1 is shown in Fig 1, in which 1 is reasonably assumed to have D_{2h} symmetry and the interatomic distances are taken according to the X-ray data of TTF and the literature by Pople et al..^{6,7}

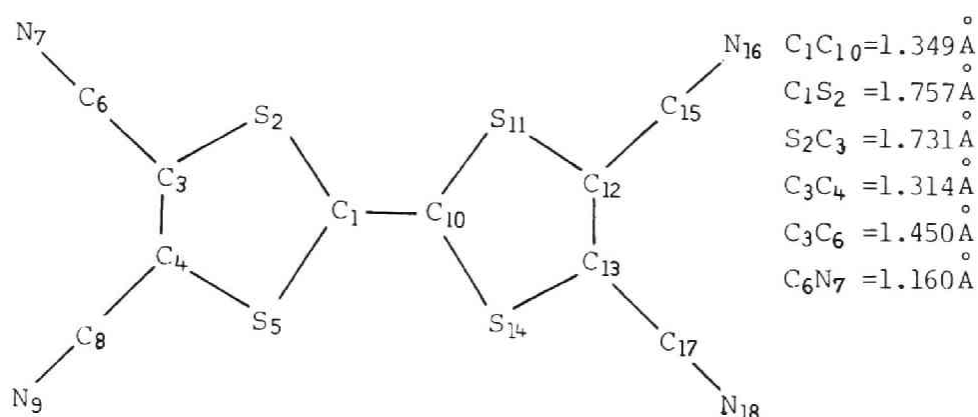


Fig. 1. Geometries of Tetracyanotetrathiafulvalene

The sulfur atom has not only 3s and 3p, but also 3d orbitals in the valence state. In the case of tetrathiafulvalene, it is pointed out that inclusion of sulfur d-orbitals is necessary to explain the relative bond lengths of the two carbon-carbon double bonds in the X-ray analysis of TTF. Accordingly, in this calculation the 3d orbitals of sulfur atom were taken into accounts.

RESULTS AND DISCUSSION

The electronic spectra of tetracyano TTF, 1, in the visible and

Table 3. Energies and Approximate Description of the Molecular Orbitals of Tetracyanotetrathiafulvalene

Energy eV	Symbol	Description	D _{2h} Symmetry label
-3.13	σ	Delocalized over bridge carbons and sulfur atoms	B _{3u}
-3.14	π		B _{1g}
-3.19	σ		A _g
-3.42	σ	Node at bridge carbons	A _g
-3.53	π	(delocalized over DCNE) *	B _{1g}
-3.54	π	Node at bridge carbons (delocalized over DCNE) *	B _{2u}

-10.47	π	Delocalized over TTF	A _g
-12.65	π	Delocalized over whole molecule	B _{3u}
-13.78	π	Node at bridge carbons** (delocalized over DTE)	B _{1g}
-13.84	π	Node at bridge carbons** (delocalized over DTE)	B _{2u}
-13.88	σ		B _{2u}
-13.93	σ		B _{2u}

*: DCNE; dicyanoethylene moiety

** : DTE ; dithioethylene moiety

ultraviolet regions were measured in benzene and in methanol. The absorption maxima, corresponding extinction coefficients, and solvents used are tabulated in Table 1. The compound, 1, shows two absorption bands in the ultraviolet region and one absorption band in the visible region. In order to assign these absorption bands, especially the band at the longest wave length, the calculations were carried out by the semiempirical ASMO-SCF and ASMO-SCF-CI methods involving all valence electrons, with the zero-differential overlap approximation adopted. The MO energies for each six occupied and vacant levels and their approximate descriptions are shown in Table 3.

The assumed geometry D_{2h} , planar ring geometry, made it possible to make distinctions between molecular orbitals constructed from in-plane atomic orbitals (σ) and molecular orbitals made up of out-of-plane atomic orbitals (π). Because of the large atomic orbital basis set (72 in the case of neglecting d orbitals on sulfur atom, 92 in the case of including d orbitals), the coefficients of the molecular orbitals were not represented.

The results of calculated singlet transition energies and oscillator strengths after the configuration interaction in the case of including d orbitals, and for comparison, the results of calculation in the case of neglecting d orbitals are represented in Table 4.

The transition energies calculated by including d-orbitals on sulfur atom were in good agreement with those observed, while in the case of neglecting d-orbitals the calculated values were prominently different from the observed ones. This clearly demonstrates that

Table 4. Calculated Transition Energies and Oscillator Strengths for
Tetracyanotetrathiafulvalene

$\Delta E_{\text{obs}}, \text{eV}$	ASMO-SCF-CI (with d)		ASMO-SCF-CI (no d)		Assignment ^b
	$\Delta E_{\text{calcd}}, \text{eV}$	f	$\Delta E_{\text{calcd}}, \text{eV}$	f	
2.48 (3.30) ^a	3.22	0.357	4.07	0.527	$\pi_{\text{TTE}} \rightarrow \pi_{\text{DCNE}}^*$
3.54 (4.18) ^a	3.36	0.656	5.80	0.506	$\pi_{\text{TTF}} \rightarrow \pi_{\text{TTE}}^*$
4.77	5.41	0.519	8.12	0.347	$\pi_{\text{TTF}} \rightarrow \pi_{\text{DCNE}}^*$
	5.75	0.130			$\pi_{\text{DTE}} \rightarrow \pi_{\text{DCNE}}^*$
	6.21	0.585			$\pi_{\text{DTE}} \rightarrow \pi_{\text{TTE}}^*$

a: The numbers in parentheses indicate $\log \epsilon_{\text{max}}$, obtained from measurements.

b: TTE; Tetrathioethylene component, DCNE; Dicyanoethylene component
TTF; Tetrathiafulvalene component, DTE; Dithioethylene component

the d-orbitals of sulfur atom significantly participate in the electronic transition of the system 1.

The longest wave length absorption band of 1 at 2.48 eV can be reasonably assigned to the excitation from the π -orbital of central tetrathioethylene component ($S_2C=CS_2$) to the π^* -orbital of dicyanoethylene component ($NC-C=C-CN$), namely to the $\pi_{TTE} \rightarrow \pi_{DCNE}^*$ transition.

Related to this correspondence, the highest occupied and lowest vacant molecular orbitals are shown in Fig 2. As seen in Fig 2, the HOMO indicates the large contribution of the tetrathioethylene component ($S_2C=CS_2$) to the π -MO, whilst the LUMO indicates the large contribution of the dicyanoethylene component ($NC-C=C-CN$) to the π^* -MO. Thus, this $\pi \rightarrow \pi^*$ transition is reasonably explained by the tran-

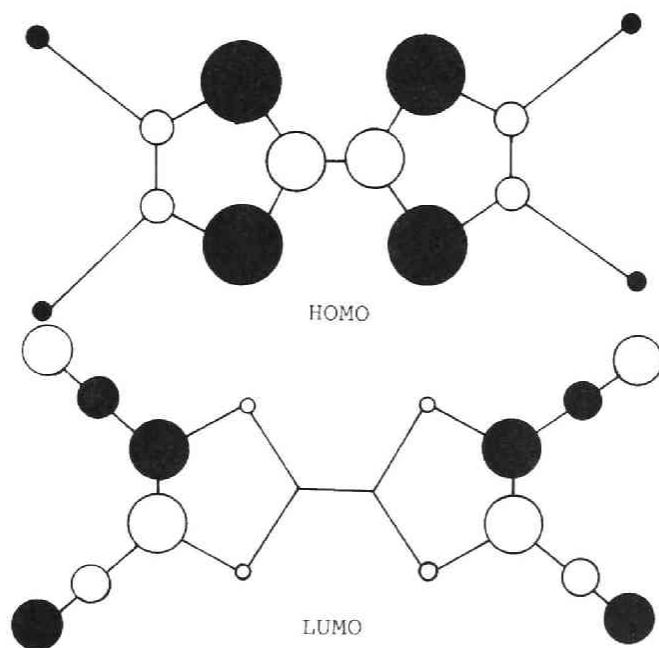


Fig. 2. Contour Map of HOMO and LUMO of Tetracyanotetrathiafulvalene.

sition from the electron rich component to the electron deficient component, just as the charge-transfer absorption band between tetrathiafulvalene and tetracyanoquinodimethane.

Consequently, the absorption band at the longest wave length is well interpreted in terms of intramolecular charge-transfer.

This interpretation is also supported by the observed results that the absorption band at the longest wave length exhibits blue shift by changing solvents from benzene (502 nm) to methanol (480 nm), which are listed in Table 5.

Table 5. Electronic Spectra (λ_{\max} in nm and $\log \epsilon_{\max}$) of 1

Solvents	A-band	B-band	C-band
benzene	502 (3.30)	328 (4.18)	
methylene chloride	500 (3.36)	325 (4.20)	262 (4.41)
acetonitrile	492 (3.30)	323 (4.16)	261 (4.33)
methanol	480 (3.39)	320 (4.04)	261 (4.20)

The absorption bands at 3.54 and 4.77 eV are reasonably assigned to the excitation from the π -orbital of tetrathiafulvalene component to the π^* -orbital of tetrathioethylene and π^* -orbital of dicyanoethylene component, respectively, namely to the $\pi_{\text{TTF}} \rightarrow \pi_{\text{TTE}}^*$ and $\pi_{\text{TTF}} \rightarrow \pi_{\text{DCNE}}^*$ transition, since there are agreements in the transition energies and strong intensities between the calculated results and observed ones.

Lastly, the charge density calculated from ASMO-SCF method is

shown in Fig 3. As seen in Fig 3, the negative charges destribute largely to the sulfur atoms, which means that the including d-orbitals have the large capacity of storing negative charges and stabilize the electronic structure in the electron rich system 1.

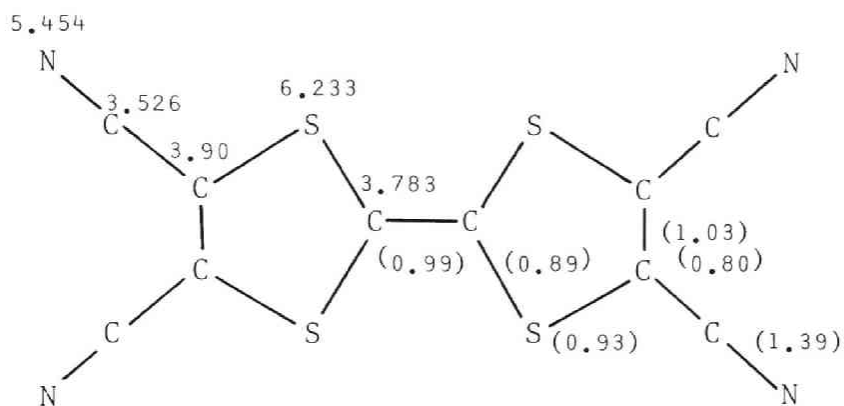


Fig. 3. Charge Density and Bond Order in Tetracyanotetrathiafulvalene by ASMO-SCF.

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CHAPTER V

CNDO/2 STUDIES ON THE REACTIONS OF THIOCARBONYL COMPOUNDS WITH TRIVALENT PHOSPHORUS COMPOUNDS

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To be published.

SUMMARY

Theoretical investigation of the reactions of thiocarbonyl compounds, aliphatic thioketones and 1,3-dithiole-2-thiones (isotrithione), by assuming two typical intermediates, betaine and phosphorane, has been carried out by the aids of CNDO/2 method. In the system of thioacetone - phosphite, the betaine is more stable than the phosphorane in the total energy, whereas in the system of 1,3-dithiole-2-thione - phosphite the phosphorane is more stable than the betaine. It was concluded that the reaction product is dependent on stability of the assumed intermediates, betaine and/or phosphorane.

INTRODUCTION

The chemistry of thiocarbonyl compounds has recently received increased interests by theoretical chemists as well as experimental chemists. Many theoretical treatments with spectral data of thiocarbonyl compounds have been reported so far.¹ However, the theoretical approach to the reactivity of thiocarbonyl compounds remains unexplored up to the present. The reactions of thiocarbonyl compounds with trivalent phosphorus compounds were studied² and described in Chapter I, II and III. In the reactions of aliphatic thioketones trialkyl phosphites attacked at the carbon atom of thiocarbonyl group and formed the betaine intermediate to give alkylthio and/or mercapto phosphonic acid esters, whilst in the reactions of electronegatively

substituted 1,3-dithiole-2-thiones (isotrithiones) trivalent phosphorus compounds attacked at the sulfur atom of isotrithiones and formed the phosphorane intermediate to give tetrathiafulvalenes.

In this chapter, in order to elucidate these interesting feature in the reaction behavior the theoretical study on the reactions of thiocarbonyl compounds with trialkyl phosphites has been carried out by the use of CNDO/2 method.³

METHOD OF CALCULATION

Calculations were carried out by means of the CNDO/2 method³, with the following parameters which are tabulated in Table.⁴ The d orbitals on sulfur and phosphorus atoms were not included in this calculation. The procedure in this study is fundamentally the optimization of the structures of reaction intermediates. That is to say, the possible geometrical structures were assumed and the most stable structures were determined by minimizing the molecular energies with respect to geometrical parameters. The systems chosen in the calculation are (i) thioacetone - phosphite, and (ii) 1,3-dithiole-2-thione - phosphite.

Geometries. The geometries of acetone and cyclohexanone were used for those of thioacetone and cyclohexanethione, respectively, except for the C=S bond distance, which was totally taken as 1.62 Å. The geometry of isotrithione was taken from the literature by Cowan et al.⁵.

In the systems of thiocarbonyl compounds with phosphite, the bond

Table 1. Parameters for CNDO/2 Calculation⁴ (β , ζ , $\frac{1}{2}(I_s + A_s)$, $\frac{1}{2}(I_p + A_p)$)

	β	ζ	$\frac{1}{2}(I_s + A_s)$	$\frac{1}{2}(I_p + A_p)$
H	-9.00	1.20000	7.176	
C	-21.00	1.62500	14.051	5.572
N	-25.00	1.95000	19.316	7.275
O	-31.00	2.27500	25.390	9.111
S [*]	-18.15	1.81667	17.650	6.989
P [*]	-15.07	1.60000	14.033	5.464

*: In this calculation d-orbitals on sulfur and phosphorus atoms were neglected, and so the parameters for 3d-orbitals are not shown.

lengths of 1.87, 1.81, 1.80, 0.92 and $2.14 \overset{\circ}{\text{\AA}}$ for C-P, C-S, P-O, O-H and P-S bonds, respectively, were estimated as the summation of covalent radius of each atom.⁶ The bond angle around the phosphorus atom was taken to be $109^{\circ}28'$ by assuming tetrahedral geometry. The bond angles and bond lengths for 1,3-dithiole were taken from the literature by Cowan et al..⁵

RESULTS AND DISCUSSION

In the first place, the charge densities and bond orders of the thiocarbonyl groups of thioacetone, cyclohexanethione, isotrithione and dicyano isotrithione obtained by CNDO/2 method with respect to the C=S bond distance $1.62 \overset{\circ}{\text{\AA}}$ are listed in Table 2. Table 2 showed the features for thiocarbonyl compounds that the π -bond of thiocarbonyl group is considerably polarized and the bond orders (0.86 – 0.89) is small compared with that of a carbonyl group (e.g. 0.93 for acetone)⁷. This fact implies that the π -bond has a zwitter-ionic character ($\text{C}^+ - \text{S}^-$) to some extent. On the other hand, σ charge density reveals the polarization in the opposite direction, different from that in carbonyl groups where both π - and σ -charge densities show the polarization in the same direction. The σ charge densities of sulfur atoms of thiocarbonyl groups are all positive, which might seemingly be the factor of thiophilic attack by nucleophiles. However, in the reaction of thioacetone and cyclohexanethione with trialkyl phosphites carbophilic attack occurred, though sulfur atoms are positively charged

Table 2. Charge Densities and Bond Orders of Thioacetone, Cyclohexanethione, Isotrithione and Dicyanoisotrithione.

		C	S	Bond order
Thioacetone	σ	-0.144	+0.162	
	π	+0.315	-0.424	0.86
	net	+0.171	-0.262	

Cyclohexane- thione	σ	-0.152	+0.161	
	π	+0.312	-0.423	0.86
	net	+0.160	-0.262	

Isotrithione	σ	-0.113	+0.252	
	π	+0.297	-0.491	0.89
	net	+0.184	-0.239	

Dicyano- isotrithione	σ	-0.109	+0.260	
	π	+0.282	-0.469	0.89
	net	+0.173	-0.209	
		C	O	
Acetone ⁷	σ	+0.07	-0.02	
	π	+0.18	-0.27	0.93
	net	+0.25	-0.29	

with respect to σ -bond, which suggests that such positive σ charge densities on sulfur atoms are not main factor of thiophilic attack by phosphites. And the net charge of thiocarbonyl group indicates slightly positive and negative charges on the carbon and sulfur atoms, respectively. As a result, such considerations with respect to the ground state can not afford significant information about the two typical reactions of thiocarbonyl compounds with phosphites, carbophilic and thiophilic attack.

In other words, the product determining step is considered not to be in the initial state, but to be reaction-proceeding state. Therefore, MO calculation was carried out to determine the most stable structure of the reaction intermediate. Two types of systems, thioacetone - $P(OH)_3$ and isotrithione - $P(OH)_3$, were chosen as the simplified models.

Thioacetone - $P(OH)_3$.

The bond angles of θ, ϕ and δ in Fig. 1 were chosen as the sign-

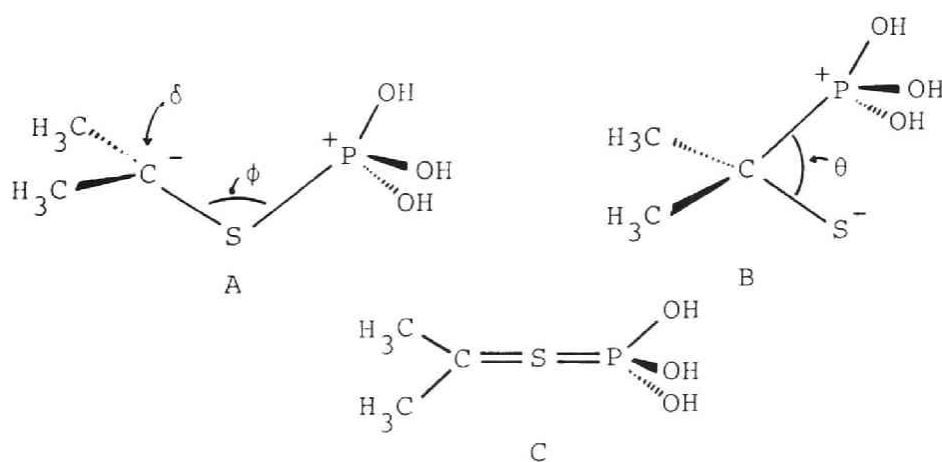


Fig.1 Structures Assumed for Thioacetone - $P(OH)_3$

ificant parameters and the other bond lengths and bond angles were taken as mentioned above. The bond angles around the central carbon atom was taken $109^{\circ}28'$.

In the betaine intermediate (B), which is formed by the carbophilic attack of phosphite, the bond angle θ ($\angle P^+-C-S^-$) was tested to change. Minimization of total energy (E_t) for B gives the smallest value of -100.367 a.u. at $\theta = 100^{\circ}$.

On the other hand, in the phosphorane intermediate (A), which is formed by the thiophilic attack of phosphite, the bond angle ϕ was firstly tested to change. Keeping tetrahedral geometry at the central carbon atom ($\delta=54^{\circ}44'$), changing the angle ϕ makes the phosphorane most stable at $\phi = 100^{\circ}$ ($E_t = -100.333$ a.u.). Further deformation with δ was carried out, and as the angle δ decrease to 0° , the total energy of the system A became larger. Considering these results, such a procedure was repeated until an absolute energy minimum was achieved. Especially, the linear phosphorane structure (C) becomes most stable as phosphorane intermediate ($E_t = -100.354$ a.u.).

Comparing the total energies of two type intermediates, the betaine intermediate B should be more stable by 0.013 a.u. (8.2Kcal) than the phosphorane intermediate A and/or C. According to the above consideration, it can be also concluded that in the reactions of aliphatic thioketones with trialkyl phosphites carbophilic attack would be more favored than thiophilic attack and the betaine intermediate would be formed to give alkylthio- and/or mercapto-phosphonic acid esters.

1,3-Dithiole-2-thione - phosphite. In this system, two type intermediates, betaine intermediate (B') and phosphorane intermediate (A'), were similarly assumed and the bond angles of α , β and γ in Fig. 2 were also chosen as the significant geometrical parameters.

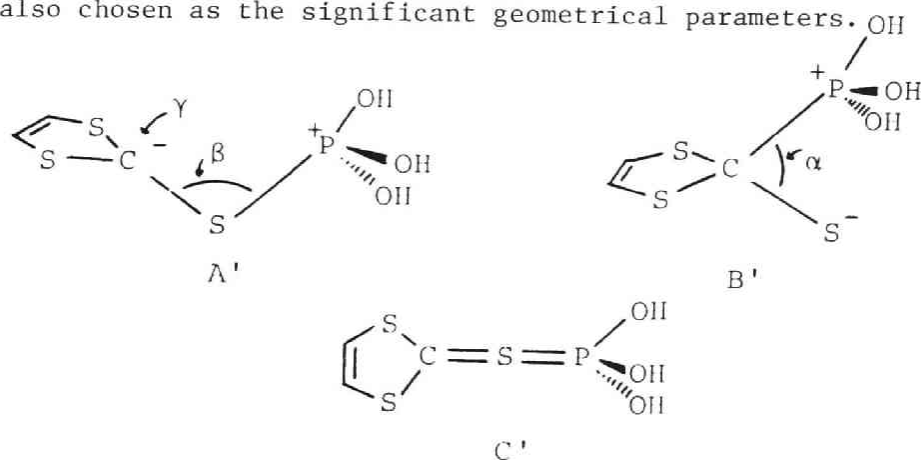


Fig.2 Structures Assumed for 1,3-Dithiole-2-thione - $P(OH)_3$.

In the betaine intermediate (B'), which is formed by the carbo-philic attack of phosphite, the bond angle α ($\angle P^+-C-S^-$) was tested to change, and the optimization gave the total energy of -118.296 a.u. at $\alpha = 100^\circ$.

In the phosphorane intermediate (A'), keeping tetrahedral geometry at the central carbon atom ($\gamma = 54^\circ 44'$), energy minimum value of -118.270 a.u. was obtained at $\beta = 100^\circ$. Further small geometrical deformation with respect to γ resulted in lowering the molecular energy: E_t at $\gamma = 44^\circ$ -118.270 a.u., $\gamma = 14^\circ$ -118.273 a.u., $\gamma = 4^\circ$ -118.276 a.u. and $\gamma = 0^\circ$ -118.278 a.u.. It is particularly interesting that the deformation from tetrahedral structure to planar with respect to the central carbon atom makes the intermediate A' more stable, which suggests that the sulfur atoms adjacent to the carbanion would

reduce negative charge by the participation of d-orbitals in the planar structure.

Considering these results, such a procedure was repeated until an absolute minimum in energy with respect to β and γ was obtained. Contrary to the case of thioacetone - phosphite, phosphorane intermediate A' became more stable than the betaine intermediate B' when γ and β are 5° and more than 150° , respectively. Especially, the most stable structure in this system was attained when γ and β are 0° and 180° , respectively, that is to say, the linear phosphorane C' is the most stable ($E_t = -118.301$ a.u.).

Though in the case of thioacetone - $P(OH)_3$ even the linear phosphorane C could not exceed the betaine intermediate B in total energy, in the system of 1,3-dithiole-2-thione - $P(OH)_3$ it can be observed that the linear phosphorane C' is the most stable structure and more stable by 0.005 a.u. (3.1Kcal) than the betaine intermediate B'. According to these results, it can be also concluded that in the reactions of substituted 1,3-dithiole-2-thiones with trivalent phosphorus compounds thiophilic attack would be more favored than carbophilic attack, and the phosphorane intermediate would be formed, which is well coincident with the experimental results.

Similar results were obtained in the system of 4,5-dicyano-1,3-dithiole-2-thione - $P(OH)_3$. The lowest total energy for the betaine intermediate was -153.977 a.u. at $\angle P^+ - C - S^- = 100^\circ$. And the lowest total energy for the phosphorane intermediate was obtained of -153.982 a.u. in the linear structure. Similar to the above system, the

phosphorane is more stable by 0.005 a.u. (3.1 Kcal) than the betaine intermediate.

Consequently, it can be concluded that the products by the reactions of thiocarbonyl compounds with phosphites are controlled by the difference in stability of the reaction intermediates, betaine and/or phosphorane.

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CHAPTER VI

REACTION OF DITHIOACETATES AND CYCLOPENTENETHIONE WITH TRIALKYL PHOSPHITES *

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* Published in Tetrahedron Lett., in press (1978).

SUMMARY

The reactions of dithioacetates with trialkyl phosphites were carried out under reflux condition. In this reaction, dithioacetates reacted with trialkyl phosphites to give thio-Claisen ester condensation type products, E- and Z-form of methyl- β -methylthio-dithio-crotonates via dehydrogen sulfide from two molecule of dithioacetates. Though the phosphites are known to behave as nucleophile to the thio-carbonyl groups, the reaction mechanism is interpreted in terms of the function of trialkyl phosphites as base. Such a dehydrogen sulfide condensation by trialkyl phosphite was also observed in the reaction of 2,3-dimethyl-cyclopent-2-ene-1-thione with trimethyl phosphite to give E- and Z-form enethione.

INTRODUCTION

It is well known that ethyl acetate gives Claisen condensation product in the presence of sodium ethoxide. Whether the similar condensation would occur when the oxygen atom of carbonyl group ($C=O$) is replaced by the sulfur atom ($C=S$) is an interesting problem to give information about the acidity of α -proton of thiocarbonyl groups. It was reported that S- and O-ethyl esters of monothioacetic acid underwent similar Claisen ester condensation to give 1,3-dicarbonyl¹ and 1,3-dithiocarbonyl compounds,² respectively. Accordingly, thio-camphor reacts with benzaldehyde yielding a simple aldol condensation

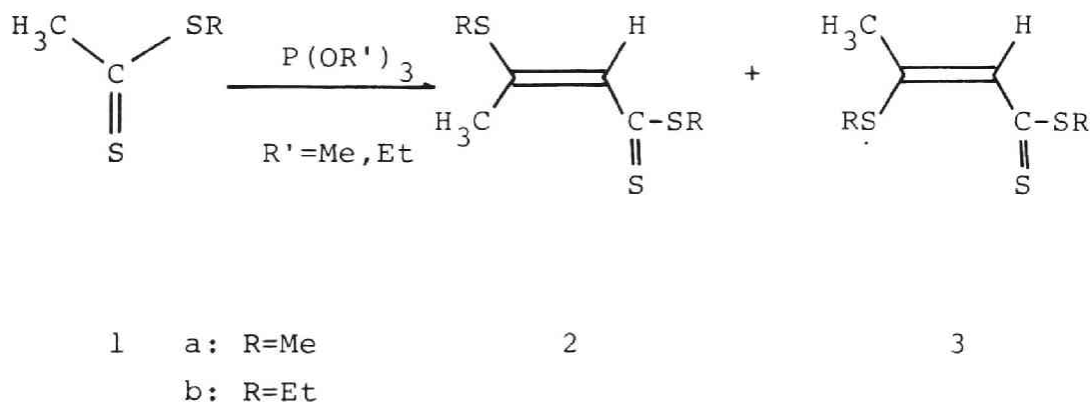
product under basic condition.³ Consequently, it is reasonably clear that α -proton of thiocarbonyl group has the acidity enough to achieve Claisen condensation and aldol condensation.

In chapter I and II, trialkyl phosphites reacts with aliphatic alkanethiones at the carbon atom of thiocarbonyl group, and in chapter III the phosphites react with 1,3-dithiole-2-thiones at the sulfur atom of thiocarbonyl group. However, trivalent phosphorus compounds have lone pair electrons on phosphorus atoms, and so phosphites may be regarded as base even though such reactions that phosphites react as base are not yet reported. In this chapter dithioacetate and 2,3-dimethyl-cyclopent-2-ene-1-thione were employed as thiocarbonyl compounds and reacted with trialkyl phosphites. In these reactions the phosphites behave as base, not nucleophile, and give condensation products.

RESULTS AND DISCUSSION

Reaction of dithioacetates with trialkyl phosphites. A mixture of methyl dithioacetate (1a) and excess trimethyl phosphite was heated to reflux temperature with stirring under argon atmosphere. The reaction was monitored by thin layer chromatograph technique, and heating was continued for 8 hr. During this period the color of the reaction mixture turned to dark red from light yellow of starting material. The reaction mixture was diluted with petroleum ether and was directly subjected to chromatograph on silica eluting with petroleum

ether. The first orange band gave red purple fraction, which gave red liquid (2a) upon evaporation. And the second red band gave pink fraction, which gave red crystal (3a).



The structures of 2a and 3a were determined by their analytical and spectral data. The pmr spectra of 2a and 3a are illustrated in Fig 1. The analytical data and mass spectra of 2a and 3a showed that both 2a and 3a have the same formula $\text{C}_6\text{H}_{10}\text{S}_3$, which indicates that 2a and 3a are isomers to each other. In the cmr spectrum of 2a, the carbon of thiocarbonyl group ($\text{C}=\text{S}$) resonated at δ 214.0 ppm and those of carbon-carbon double bond at δ 157.0 ($\text{C}=\text{C}-\text{H}$) and 129.0 ($\text{C}=\text{C}-\text{H}$) ppm, which clearly represents the presence of the enethione moiety ($\text{C}=\text{C}-\text{C}=\text{S}$). The infrared spectra of 2a and 3a revealed absorptions at 1555 and 1515 cm^{-1} attributable to carbon-carbon double bond conjugated to thiocarbonyl group, and at 1228 and 1239 cm^{-1} assigned to thiocarbonyl group, respectively, which also indicate the presence of enethione moiety. The pmr spectrum of 2a consisted of four kinds of singlets at δ 2.40(SCH_3), 2.55($=\text{C}-\text{CH}_3$), 2.61(CS_2CH_3) and 6.52($\text{C}=\text{C}-\text{H}$) ppm. On the other hand, the pmr spectrum of 3a consisted of four

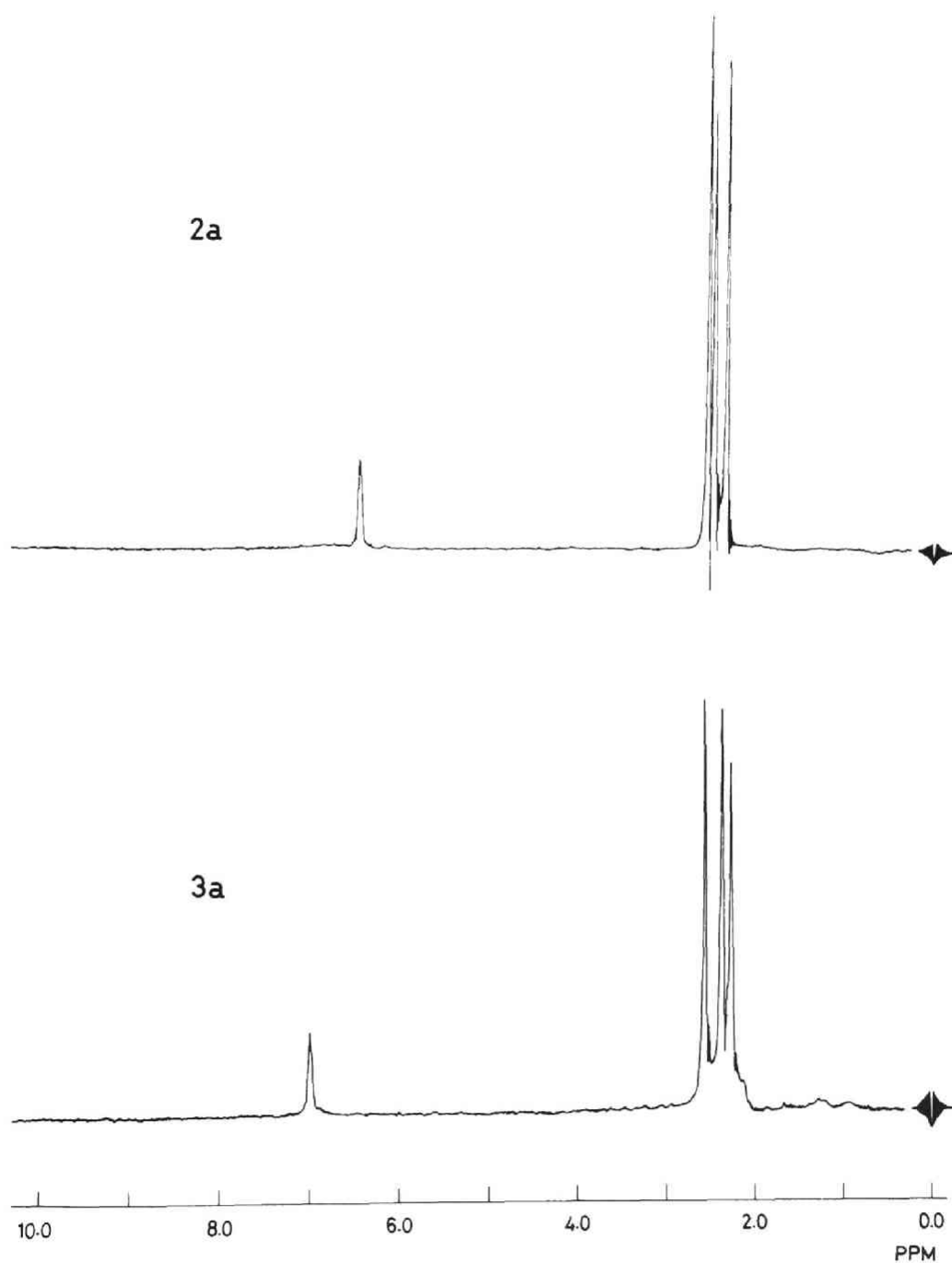


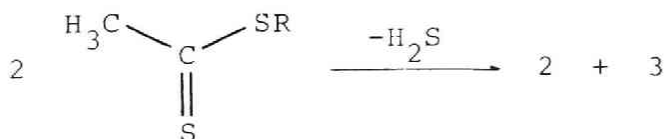
Fig. 1. Comparison of ^1H -NMR Spectra of 2a and 3a.

singlets at δ 2.28(=C-CH₃), 2.39(SCH₃), 2.60(CS₂CH₃) and 7.00(C=C-H) ppm. Comparing the chemical shifts of methyl protons attached to the carbon-carbon double bond, that of 2a appeared at lower field (δ 2.55) than that of 3a (δ 2.28). Taking the magnetic anisotropy of thiocarbonyl groups into accounts, the lower chemical shift of methyl protons of 2a indicates that the methyl group and the thiocarbonyl group are situated in the same side of carbon-carbon double bond. Also comparing the chemical shifts of olefin protons, that of 2a appeared at higher field (δ 6.52) than that of 3a (δ 7.00), which can be reasonably explained by the effect of the lone pair electrons of sulfur atom of methylthio group. That is to say, the stereochemistry of 2a and 3a is assigned to (E)-form and (Z)-form, respectively. However, the pmr spectrum of 2a (or 3a) changed to that of a mixture of 2a and 3a (1:1) at room temperature after 1 day.

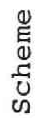
The reaction of ethyl dithioacetate (1b) with trimethyl phosphite was similarly carried out and monitored by thin layer chromatography and heating was continued for 10 hr. During this period the color of the mixture turned to dark red. The mixture was subjected to column chromatograph. After recovery of starting material, the first orange band gave red liquid (2b). The second red band gave red liquid (3b). The structures of 2b and 3b were determined in a similar manner as above. The mass spectra of 2b and 3b showed that both 2b and 3b are isomers. The infrared spectra of 2b and 3b revealed absorptions at 1550 and 1520 cm⁻¹ attributable to carbon-carbon double bond conjugated to thiocarbonyl group, and at 1220 and 1235

cm⁻¹ assigned to thiocarbonyl group, respectively. These absorptions reasonably indicate the presence of enethione moiety. The pmr spectrum of 2b consisted of two ethyl groups, methyl protons attached to carbon-carbon double bond at δ 2.48 ppm and olefin proton at δ 6.51 ppm. On the other hand, the pmr spectrum of 3b also consisted of two ethyl groups, methyl protons at δ 2.28 ppm and olefin proton at δ 6.93. Similarly, taking the anisotropy of thiocarbonyl group and sulfur atom, the stereochemistry of 2b and 3b is assigned to (E)-form and (Z)-form, respectively.

These products, 2 and 3, can be considered as thio-Claisen type condensation products of dithioacetate by elimination of hydrogen sulfide.

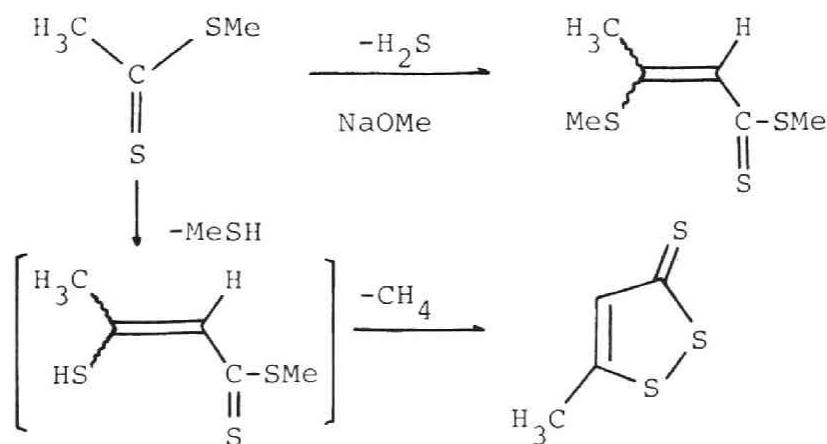


Generally, in the reactions of thiocarbonyl compounds with trialkyl phosphites, phosphites are known to behave as nucleophile. However, in this reaction trimethyl phosphite does not behave as nucleophile, but as base for its lone pair electrons. That is to say, as seen in the following reaction scheme, trimethyl phosphite should abstract α -proton of dithioacetate and form the anion (A). The resulting anion would react with another dithioacetate at thiocarbonyl carbon atom to form anion (B). The anion B and $\text{HP}^+(\text{OMe})_3$ would afford the dimer (C). With respect to the dimer C, two isomers, namely R- and S-dimers, would be formed in the reaction of anion A with another



dithioacetate. And the tautomeric ketene dithiohemiacetal type dimer would undergo dehydrogen sulfide via cyclic concerted mechanism to result in the formation of 2 and 3. That is to say, the formation of 2 and 3 is interpreted in terms of dehydrogen sulfide from R- and S-dimer, respectively. However, the mechanism, in which only one product would be formed and converted to the mixture of 2 and 3, could not be excluded owing to the fact that the pmr spectrum of 2 (or 3) changed to that of a mixture of 2 and 3 (1:1). The phosphite may participate in this dehydrogen sulfide reaction as catalyst.

As an evidence that phosphites behaved as base, it is reported by Mayer et al.⁴ that 1a gave a mixture of 2a and 3a in 18% yield in the presence of methanol free sodium methoxide as base together with 1,2-dithiole-3-thione.



But the yields of 2a and 3a are better when trimethyl phosphite was used as mild base. However, they obtained 5-methyl-1,2-dithiole-3-thione and suggested the demethane mechanism from usual thio-Claisen condensation 1,3-dithiocarbonyl compound. In the case of the reaction

with trimethyl phosphite, the ester condensation product from the anion B might be afforded, but in general such β -dithiocarbonyl compounds are known to be unstable. Therefore in this reaction condition, in the presence of trimethyl phosphite, 1,3-dithiocarbonyl compounds would react with phosphite and so could not be detected. The use of trialkyl phosphites other than trimethyl phosphite also yielded the same products, 2 and 3, but did not enhance the yields.

Though similar reaction of methyl dithiophenylacetate with trimethyl phosphite was examined, such reaction was not observed in spite of the increased acidity of α -proton. This resistance to proton abstraction may be explained in terms of steric bulkiness of phenyl group to the attack of phosphite. Accordingly, in the case of thioacetomorpholide no reaction occurred probably because of its canonical structure ($S^{-}-C=N^{+}$).

Reaction of 2,3-dimethyl-cyclopent-2-ene-1-thione. A mixture of 2,3-dimethyl-cyclopent-2-ene-1-thione (4) and excess trimethyl phosphite was heated at reflux temperature under nitrogen. The reaction was monitored by thin layer chromatograph technique and heating was continued for 2 days. After evaporation of excess trimethyl phosphite, the reaction mixture was chromatographed on silica. The greenish-yellow fraction upon evaporation gave greenish brown needles (5) in 10% yield. The following red fraction gave the dimer of 4. The structure of 5 was determined by its spectral and analytical data.

The analytical and mass spectrum data of 4 showed that 5 has the formula $C_{14}H_{18}S$. In the cmr spectrum of 4, shown in Fig 2, the

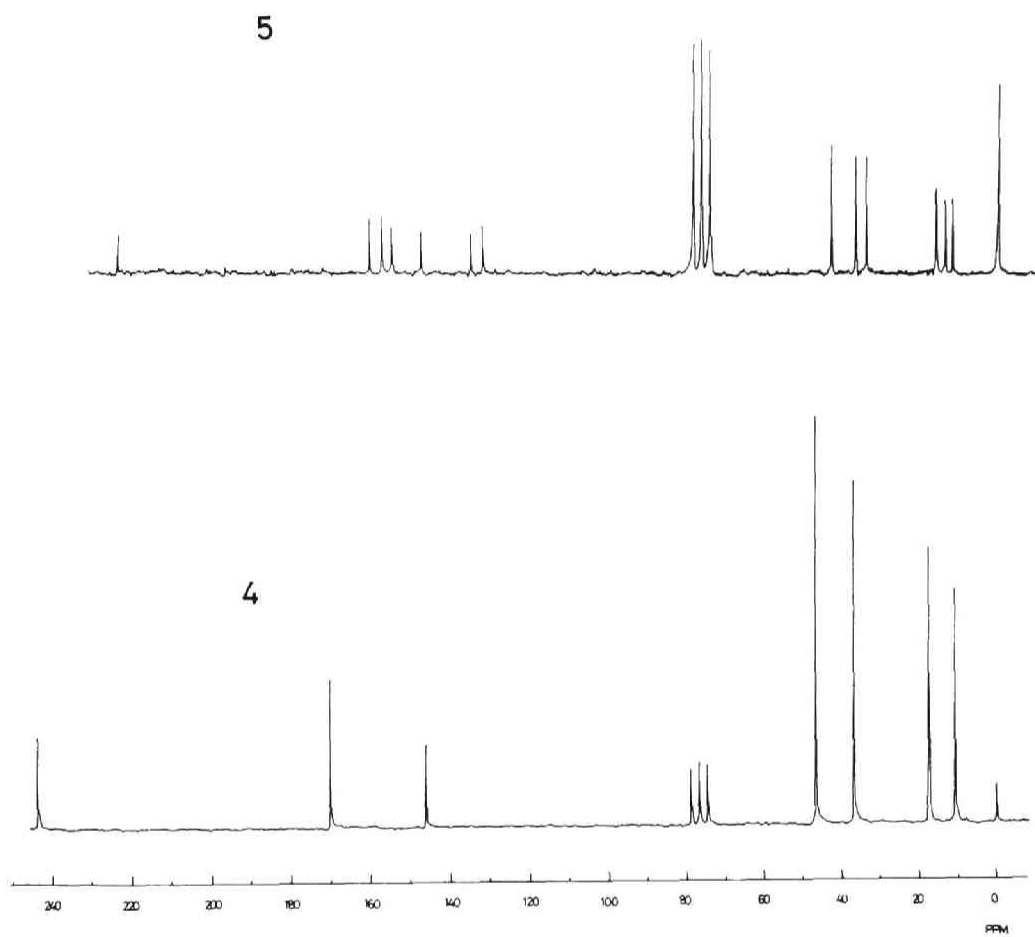
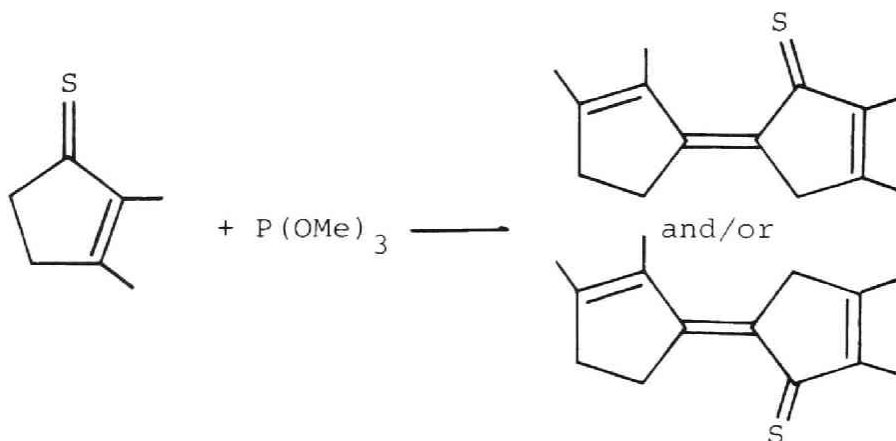
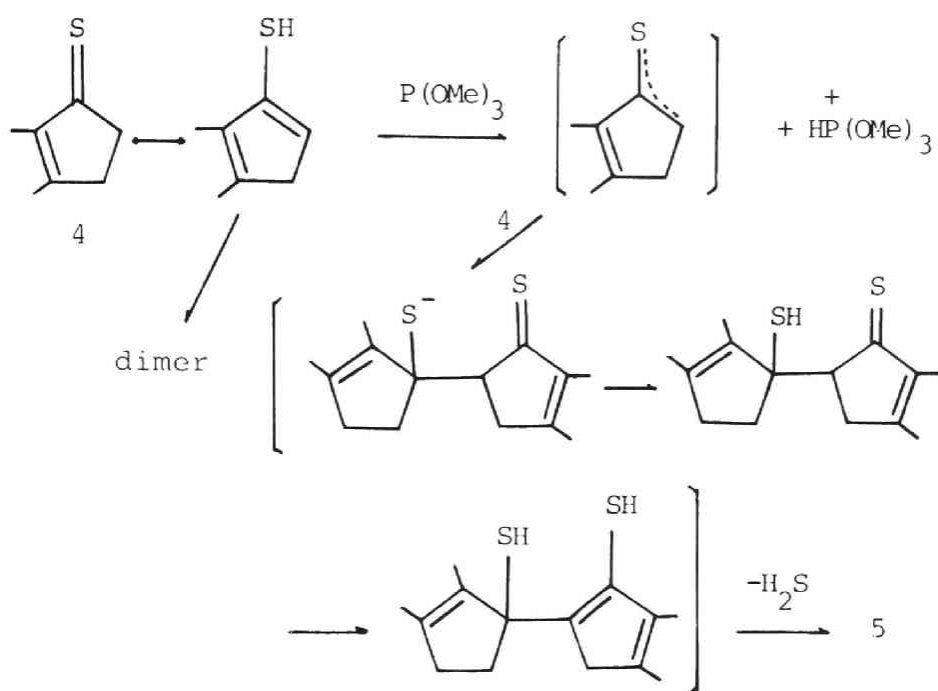


Fig. 2. Comparison of ^{13}C -NMR Spectra of 5 and 4.

carbon of the thiocarbonyl group ($C=S$) resonated at δ 226.5 ppm and those of six kinds of carbon-carbon double bonds and those of three allylic methylenes and of four methyl groups, which clearly indicates the presence of enethione moiety. Accordingly, the infrared spectrum revealed absorptions at 1624 and 1560 cm^{-1} attributable to carbon-carbon double bond (the latter should be conjugated to thiocarbonyl group) and $1245\text{ (C=S)}\text{ cm}^{-1}$. The pmr spectrum was consisted of four kinds of methyl protons and three kinds of allylic methylene protons. However, the stereochemistry of 5 could not be determined.

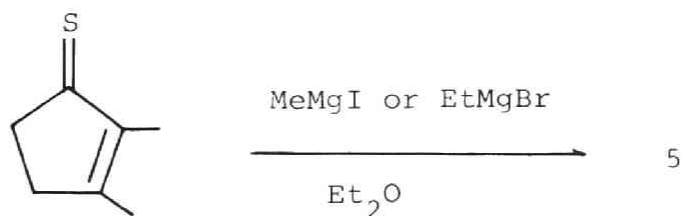


Taking those spectral data into accounts, 5 was determined as the condensation product of 4 by dehydrogen sulfide. This product 5 can also be considered as aldol type condensation product. As mentioned in the reaction of dithioacetate, phosphite should behave as base and abstract α -proton of thiocarbonyl group and form the anion D. The proton abstraction would take place from the enol type 4' (1,2-dimethyl-3-mercapto-cyclopenta-1,3-diene), since at high temperature 4 proceeded the Diels-Alder reaction to give the dimer. This dimerization and the weak basicity of trimethyl phosphite would be the rea-



son for low yield of 5. The resulting anion D would react with another 4 at thiocarbonyl carbon atom and yield anion E, which would interact with $HP^+(OMe)_3$ and afford the dimer F (not Diels-Alder type dimer). Dehydrogen sulfide from F should afford the aldol condensation type product 5.

When Grignard reagents, $MeMgI$ or $EtMgBr$, were reacted with 4, the aldol condensation product 5 was also obtained in 80-83% yield.



It is known that the Grignards generally react with thiocarbonyl

compounds at the sulfur atom of thiocarbonyl group.⁵ For example, even in the reaction of 3,4,4-trimethyl -cyclopent-2-ene-1-thione with Grignard reagents, such thiophilic attack occurred and gave desulfurized dimer in 60% yield together with S-alkylated and SH products.⁶ However, in the case of the reaction of 4 with Grignards such S-alkylated product was not observed. Therefore, in this case Grignards seemed to behave as base (proton-abstracting reagent) and give 5 via similar mechanism mentioned above.

EXPERIMENTAL

Melting points were determined using a Buchi melting apparatus in sealed tubes and are uncorrected. The infrared spectra were determined on Hitachi grating infrared spectrophotometer, Model 215, the pmr spectra were recorded on a Varian Associate AH-100 spectrometer, the cmr spectra were recorded on JEOL FX-60 spectrometer and the mass spectra were determined on Hitachi RMU-6C or RMS-4 mass spectrometer. Elemental analyses were carried out at the Elemental Analytical Center of Kyoto University. Kieselgel 60 F₂₅₄ (Merck) was used for thin layer chromatography. Wakogel C-200 was used for the absorbent of column chromatography.

Materials. Methyl dithioacetate (1a) was prepared as follows. To thioacetomorpholide in acetone, prepared from acetomorpholide and P₄S₁₀ in DME, methyl iodide was added and heated to reflux to precipitate the crystals, which was added to dry pyridine and hydrogen sul-

fide was passed at 0°C for 3 hr. The deep yellow solution was poured into cooled dil. hydrochloric acid and extracted with ether. The extract was dried over Na_2SO_4 , concentrated and distilled to give 1a in 85% yield. Ethyl dithioacetate (1b) was prepared as described by Pinner and Klein⁷ from ethyl thioimidoacetate and hydrogen sulfide in pyridine. 2,3-Dimethyl-cyclopent-2-ene-1-thione (4) was prepared from 2,3-dimethyl-cyclopent-2-enone, hydrogen sulfide and hydrogen chloride according to the literature of Metzner and Vialle.⁸ Trimethyl and triethyl phosphites were commercial materials and were used after distillation.

Reaction of methyl dithioacetate with trimethyl phosphite. A mixture of 2.04 g of 1a and 4.0 g of trimethyl phosphite was stirred and heated to reflux temperature under argon atmosphere. The reaction was monitored by thin layer chromatography and heating was continued for 8 hr. The dark red reaction mixture was added directly to 4 ml of petroleum ether and was chromatographed on silica eluting with petroleum ether. The initial yellow band led to recovery of 0.47 g of 1a. The orange band gave red purple fraction, which afforded 0.20 g of (E)-methyl (β -methylthio)-dithiocrotonate (2a) upon evaporation: yield 15%; ir (neat) 1555(C=C) and 1228(C=S) cm^{-1} ; pmr (CCl_4) δ 2.40(s, 3H, SCH_3), 2.55(s, 3H, C=C- CH_3), 2.61(s, 3H, CS_2CH_3) and 6.52(s, 1H, C=C-H); cmr (CDCl_3) δ 22.8, 24.5(SCH_3), 129.0(C=C-H), 157.0(C=C-H) and 214.0(C=S); mass m/e 178(M^+), 163, 131.

Anal. Calcd for $\text{C}_6\text{H}_{10}\text{S}_3$: C, 40.41; H, 5.65; S, 53.94.

Found: C, 40.69; H, 5.76; S, 53.81.

Next red band gave pink fraction, which afforded on evaporation 0.19 g of (Z)-methyl (β -methylthio)-dithiocrotonate (3a): mp 56–57°C; yield 13.9%; ir (KBr) 1515(C=C), 1239(C=S) and 1120 cm^{-1} ; pmr (CCl_4) δ 2.28(s, 3H, C=C-CH₃), 2.39(s, 3H, SCH₃), 2.60(s, 3H, CS₂CH₃) and 7.00(s, 1H, C=C-H); mass m/e 178(M⁺), 163, 131.

Anal. Calcd for C₆H₁₀S₃: C, 40.41; H, 5.65; S, 53.94.

Found: C, 40.57; H, 5.67; S, 53.99.

Reaction of ethyl dithioacetate with trimethyl phosphite. A mixture of 2.10 g of 1b and 4.0 g of trimethyl phosphite was heated at reflux temperature under argon for 10 hr and treated in a similar manner as above. After recovery of 1.16 g of 1b, the orange band gave 0.10 g of 2b: yield 12.3%; ir (neat) 1550(C=C) and 1220(C=S) cm^{-1} ; pmr (CCl_4) δ 1.32(t, 3H, J=7.5Hz, SCH₂CH₃), 1.38(t, 3H, J=7.1Hz, CS₂CH₂CH₃), 2.48(s, 3H, C=C-CH₃), 2.87(q, 2H, J=7.5Hz, SCH₂CH₃), 3.19(q, 2H, J=7.1Hz, CS₂CH₂CH₃) and 6.51(s, 1H, C=C-H); mass m/e 206(M⁺), 177.

Anal. Calcd for C₈H₁₄S₃: C, 46.55; H, 6.84; S, 46.61.

Found: C, 46.32; H, 7.12; S, 46.28.

Next red purple band gave 0.11 g of 3b: yield 13.9%; ir (neat) 1520(C=C), 1235(C=S) and 1109 cm^{-1} ; pmr (CCl_4) δ 1.31(t, 3H, J=7.3Hz, SCH₂CH₃), 1.35(t, 3H, J=7.1Hz, CS₂CH₂CH₃), 2.28(s, 3H, C=C-CH₃), 2.89(q, 2H, J=7.3Hz, SCH₂CH₃), 3.22(q, 2H, J=7.1Hz, CS₂CH₂CH₃) and 6.93(s, 1H, C=C-H); mass m/e 206(M⁺), 177.

Anal. Calcd for C₈H₁₄S₃: C, 46.55; H, 6.84; S, 46.61.

Found: C, 46.29; H, 6.95; S, 46.81.

Reaction of 2,3-dimethyl-cyclopent-2-ene-1-thione with trimethyl phos-*

phite. A mixture of 0.56 g of 4 and 10 ml of trimethyl phosphite was heated at reflux temperature under nitrogen for 24 hr. After evaporation of excess trimethyl phosphite, the residue was subjected to chromatograph on silica eluting with benzene. The yellow fraction was concentrated and followed by recrystallization from n-hexane to afford 0.05 g of dark brown needles: 5; mp 137-138.5°C; yield 10.3%; ir (KBr) 1624, 1560(C=C) and 1245(C=S) cm^{-1} ; cmr (CDCl_3) δ 11.8, 13.8, 15.9, 16.2(CH_3), 34.3, 37.0, 43.2(CH_2), 133.4, 136.5, 149.3, 156.8, 159.3, 162.5(=C) and 226.5(C=S) ppm; mass m/e 218(M^+).

Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{S}$: C, 77.01; H, 8.31; S, 14.68.

Found: C, 77.06; H, 8.34; S, 14.71.

Reaction of 4 with Grignard reagents. To a solution of 6 mmole of MeMgI or EtMgBr in 5 ml of ether was added dropwise 0.48 g of 4 in 8 ml of ether under nitrogen at room temperature. After addition was complete, the mixture was allowed to stand for 3 hr at room temperature and saturated aq. NH_4Cl was added and extracted with ether for several times. The red extract was dried, concentrated and subjected to column chromatography to afford 0.38 g of 5 (83%). The spectral and analytical data were all consistent with the product obtained in the reaction with trimethyl phosphite.

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Submitted to Tetrahedron.

8. Reaction of Aliphatic Thioketones with Trialkyl Phosphites

S. Yoneda, T. Kawase and Z. Yoshida

Submitted to J. Org. Chem..

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1. Reaction of Cyclohexanethione with Trialkyl Phosphites
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